Kinetic Studies of [3+2] Cycloaddition of Fischer Carbene Complexes with Nitrones

by

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To my family,

with love.

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ABBREVIATION

Anal.	analytical
bp	boiling point
^{t}Bu	*tert*-butyl
^{o}C	degree Celsius
ca.	approximately
Calcd	calculated
CAN	ceric ammonium nitrate
d	day(s)
Decomp	decompose(s)
DMSO	dimethyl sulfoxide
equiv	equivalence
cm^{-1}	per centimeter
g	gram(s)
h	hour(s)
HOMO	highest occupied molecular orbital
Hz	hertz
IR	infra-red
J:	coupling constant
L	liter
LUMO	lowest unoccupied molecular orbital
Max	Maximum
mL	milliliter
mo	month
M	moles per liter
M^{+}	molecular ion
Me	methyl
M/z	mass per charge ratio
min	minute(s)
mmol	millimole(s)
mp	melting point
NMR	nuclear magnetic resonance
Ph	phenyl
ppm	part per million
R_f	retenetion factor
r.t.	room temperature
THF	tetrahydrofuran
TMS	trimethylsilyl

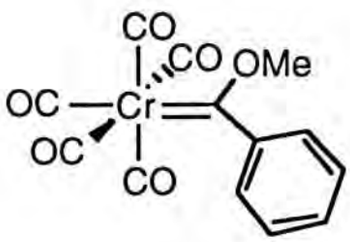
ABSTRACT

Alkynyl Fischer carbene complexes **31a-d** were found to undergo chemoselective, regioselective, and rate-enhanced 1,3-dipolar cycloaddition with *N*-*tert*-butyl nitrone (PBN) **35** to give 2,3-dihydroisoxazole carbene complexes **40** & **41** in excellent yields. These alkynyl carbene complexes can serve as synthons for substituted propiolate esters since the metal pentacarbonyl group of the cycloadducts can be easily oxidatively removed by DMSO. The reactivity of *N*-alkyl nitrones **32-36** towards carbene complexes was in the order: *N*-Me > *N*-Bn > *N*-^{t}Bu. Kinetics of the cycloaddition between carbene complexes with various substituted nitrones in different solvents have been studied. The reaction was found to be first-order in both carbene complex and nitrone. The rate enhancement of carbene complex over the corresponding organic ester **34** was estimated to be about 10^4. The reaction was controlled by HOMO(nitrone) - LUMO(carbene complex) interaction, it was consistent with the substitutent effect on nitrone: the reaction was accelerated by electron donating group in nitrone. The lack of solvent dependence and large negative entropy of activation (ca. -150 $Jmol^{-1}K^{-1}$) might suggest the reaction is a concerted one.

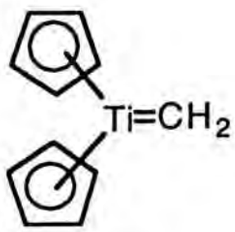
CONTENTS

I. INTRODUCTION

The first transition metal carbene complex is the phenyl methoxy carbene complex **1** prepared by E. O. Fischer in 1964.[1] Since then, carbene complexes have been examined with potential applications in organic synthesis, and the growth in the number of useful applications has increased exponentially with time.[2-4] There are two types of transition metal carbene complexes; those which have electrophilic carbene carbons attaching heteroatoms and which are typified by the pentacarbonylchromium complex **1** (Fischer carbene complex), and those which have nucleophilic carbene carbons and which are typified by the biscyclopentadienyltitanium complex **2**. Complexes **1** and **2** are often referred to as 'carbene' and 'alkylidene' complexes, respectively. Both of these names are misleading in that there has never been a reaction for any of these complexes for which the intermediacy of a free carbene has been demonstrated.



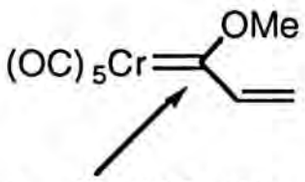
1
A Fischer carbene complex



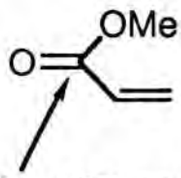
2
An alkylidene complex

The Fischer type carbene complexes are convenient to use in that they are generally crystalline solids that are handleable in air and can tolerate temperatures of 80 ^{o}C or more. They are stable to mild aqueous acids and bases and are soluble in most organic solvents even in non-polar hexane. Despite their solubility in hexane, Fischer carbene complexes such as **1** have large dipole moments and the carbene carbon displays marked electrophilic behavior. Most of the reactions of Fischer carbene complexes can be anticipated from the reaction chemistry of esters where the chromium pentacarbonyl moiety is formally replaced by an oxygen atom. The chemical and

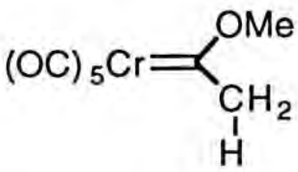
physical properties of esters reflected in these complexes are also usually greatly emphasized (Scheme I). For example, the shift of the carbene carbon in the ^{13}C NMR spectrum of the vinyl complex **3** is 323 ppm downfield from TMS (in the range of carbonium ions), while the shift of the carbonyl carbon of methyl acrylate **4** is only 167 ppm. However, the reasons of this great downfield shift of the carbene carbon are not clearly revealed.[5] Besides, the tremendous thermodynamic acidity of the α protons (pKa = 8) in **5**, which makes it more acidic than its corresponding ester **6** (pKa = 25) by 17 order of magnitude.[6] These observations point out that the chromium pentacarbonyl moiety possesses a greater electron withdrawing ability over the oxygen atom of the organic ester, and therefore suggest the vinylcarbene complex **3** would be a more reactive dienophilie over methyl acrylate **4**.



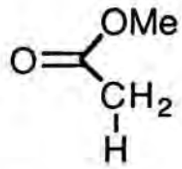
3 δ = 323 ppm



4 δ = 167 ppm



5 pKa = 8

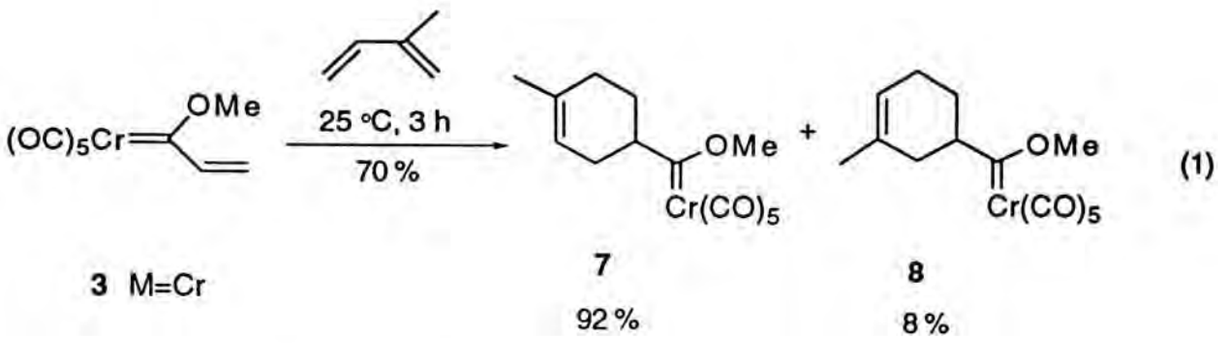


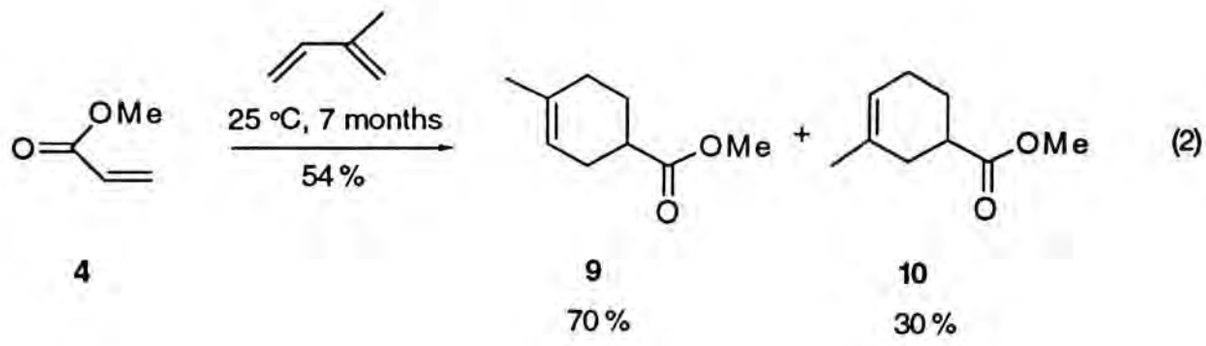
6 pKa = 25

Scheme I

Wulff and Yang were the first to report that the α,β-unsaturated Fischer carbene complex will undergo [4+2] cycloadditions with a variety of dienes with rate accelerations 10^4 order greater than that of methyl acrylate (Scheme II), their closest carbon analogue, and, as could be anticipated, there was an associated increase in the

regioselectivity.[7] Methyl acrylate **4** was found to react with isoprene in 7 months at 25 °C to give a mixture of isomers **9** and **10** (70 : 30) in 54 % yield (eq 2).[8] However, the chromium carbene complex **3** reacted with isoprene in 3 h at 25 °C to give 70 % yield of isomers **7** and **8** as a 92 : 8 mixture (eq 1). In fact, the chromium pentacarbonyl moiety always acts as a reactivity and selectivity auxiliaries in this kind of reaction.

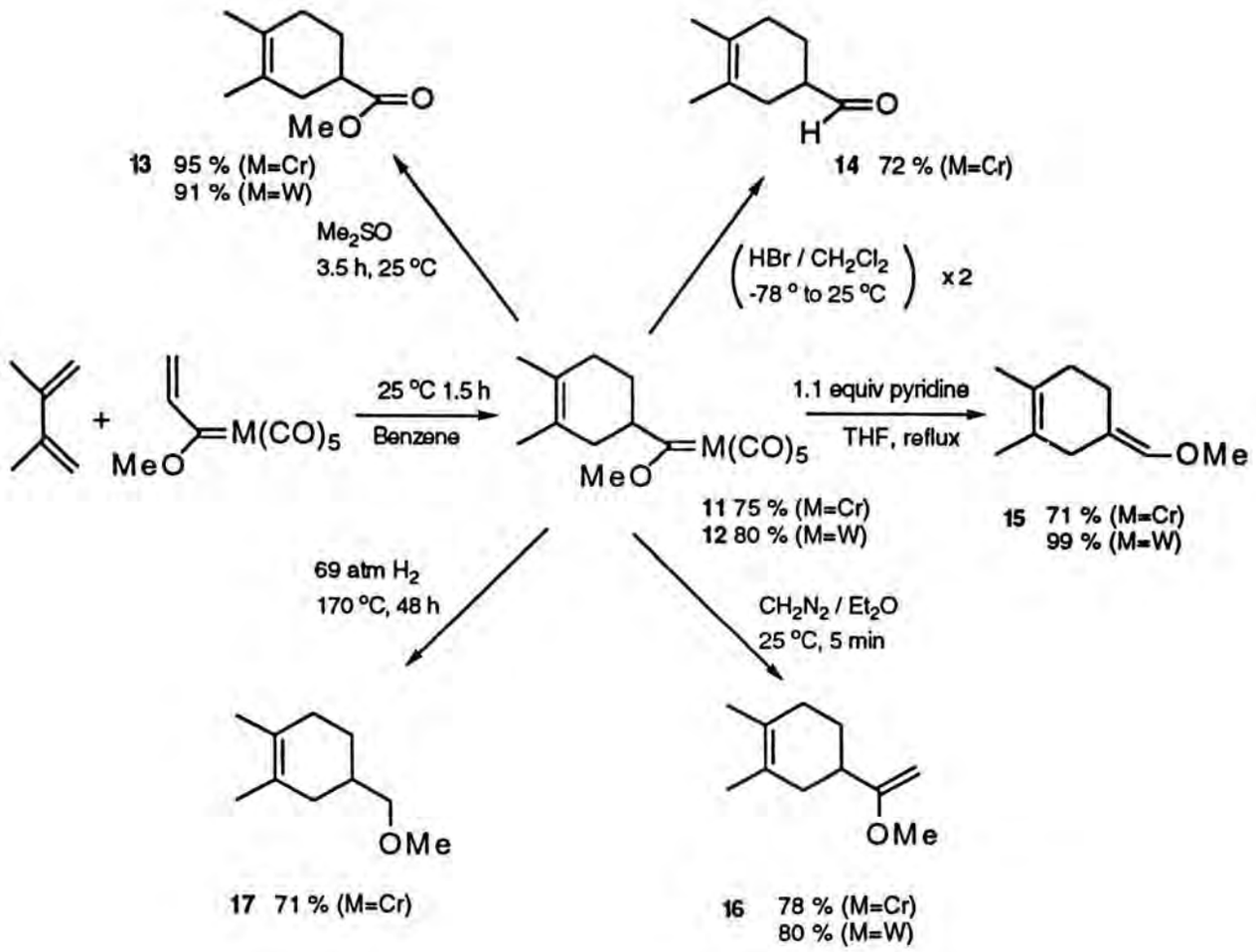




Scheme II

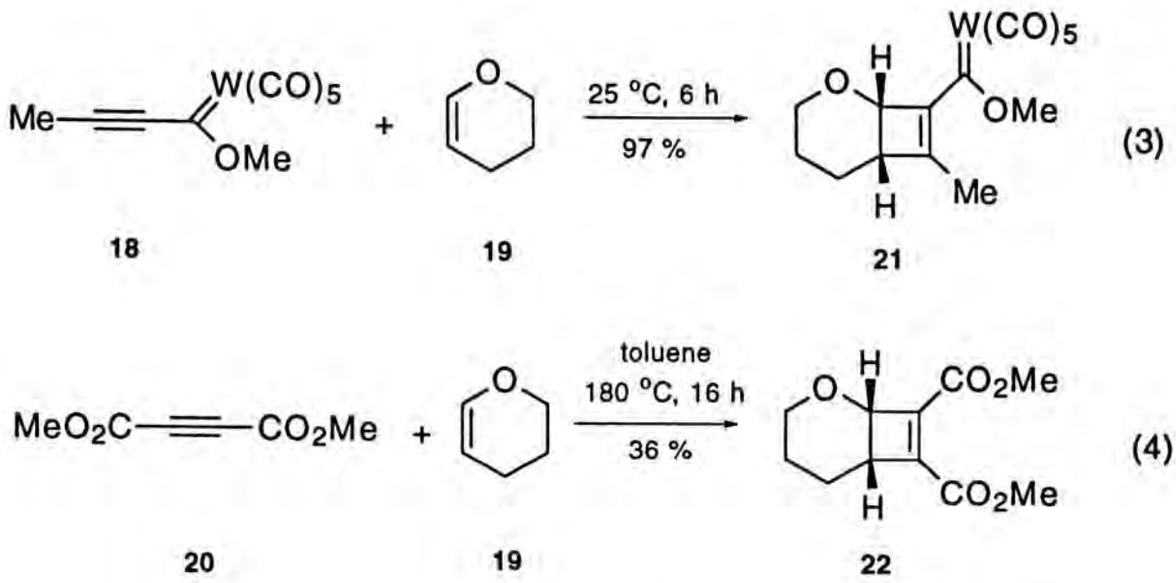
It is interesting to note that the increased reactivities in the reaction of these complexes with isoprene were comparable to those of the aluminium chloride catalysed reaction of methyl acrylate and isoprene.

By employing known reactions of Fischer carbene complexes, the cycloadduct carbene complexes can be subsequently converted into a variety of organic functional groups. Wulff examined a few of these methods for the chromium and tungsten adducts **11** and **12** (Scheme III).



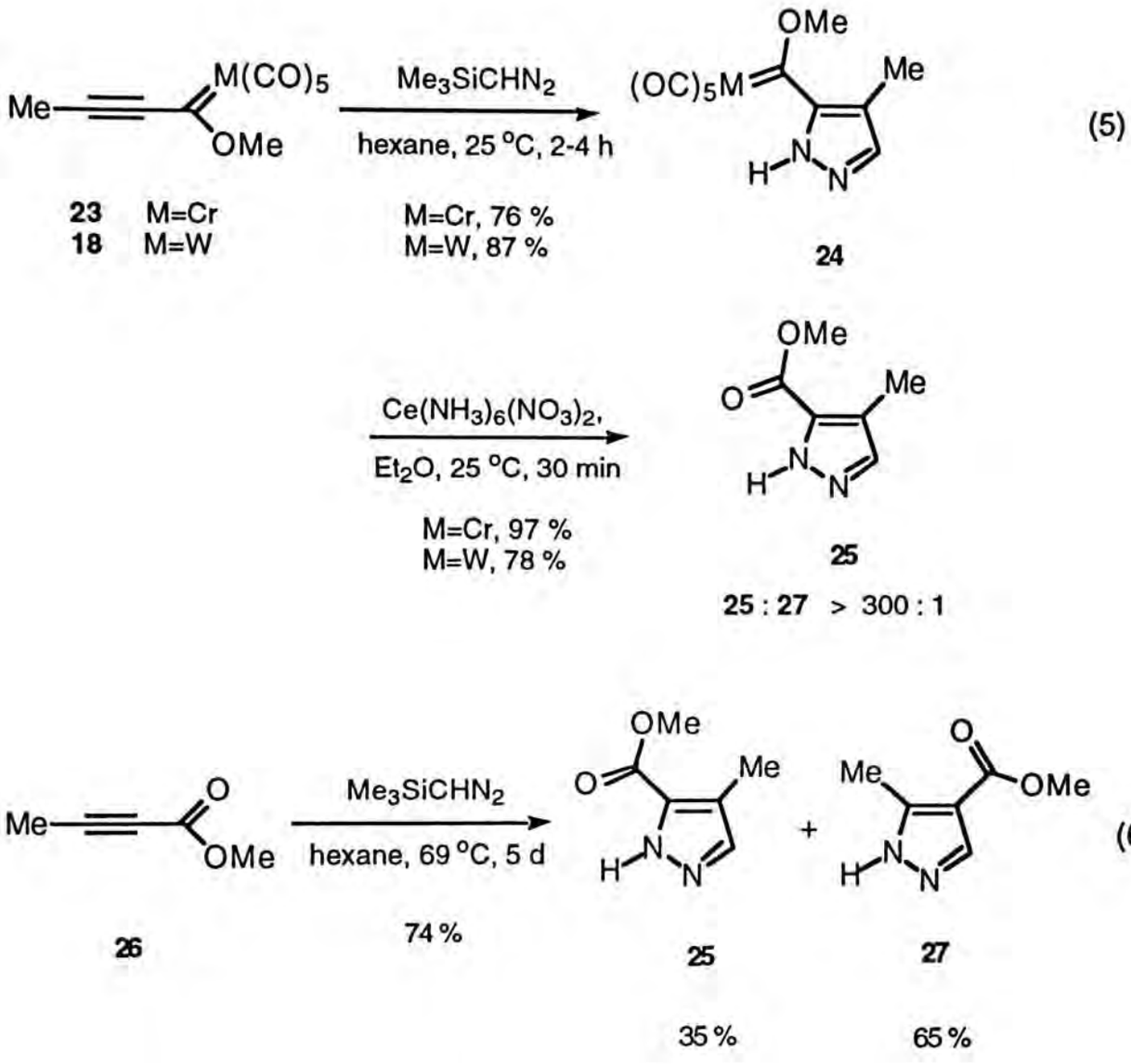
Scheme III

Apart from the [4+2] cycloaddition, the first example of [2+2] cycloaddition at the unsaturated substituent on a carbene complex has been recently reported by Wulff and Faron (Scheme IV).[9] In the example, the alkynyl tungsten carbene complex **18** reacted rapidly with enol ether **19**. While the [2+2] cycloaddition between methyl tetrolate and dihydropyran **19** is unknown, a comparison can be made between the carbene complex **18** and the doubly activated alkynyl ester **20** with the same substrate **19**. For **20**, a yield of 36 % was reported after 16 h at 180 °C in toluene (eq 4),[10] whereas 97 % yield was reported for **18** for 6 h at room temperature (eq 3). The latter reaction was proposed to involve a nonpolar concerted, synchronous one-step mechanism.[11]



Scheme IV

The [3+2] cycloaddition reactions with 1,3-dipoles have been intensely investigated in the last two decades[12] and their importance in natural product synthesis has been thoroughly established.[13] By the virtue of α,β-unsaturated Fischer carbene complexes, it is attractive to apply the complexes in synthesis of five-membered heterocyclic compounds in a rate-accelerating and highly regio- and stereoselective manner. However, there are only a few examples of [3+2] cycloaddition of Fischer carbene complexes with 1,3-dipoles. Diazoalkanes, the first 1,3-dipole, was observed to undergo cycloaddition with alkynyl carbene complexes to form the pyrazolylcarbene complexes **24** in high yield (Scheme V, eq 5).[14] The reaction was highly regioselective (**25** : **27** > 300 : 1) and in great rate enhancement in comparison with the organic ester **26** (eq 6).



23 M=Cr
18 M=W

M=Cr, 76 %
M=W, 87 %

24

(5)

M=Cr, 97 %
M=W, 78 %

25

25 : **27** > 300 : 1

26

74 %

25

35 %

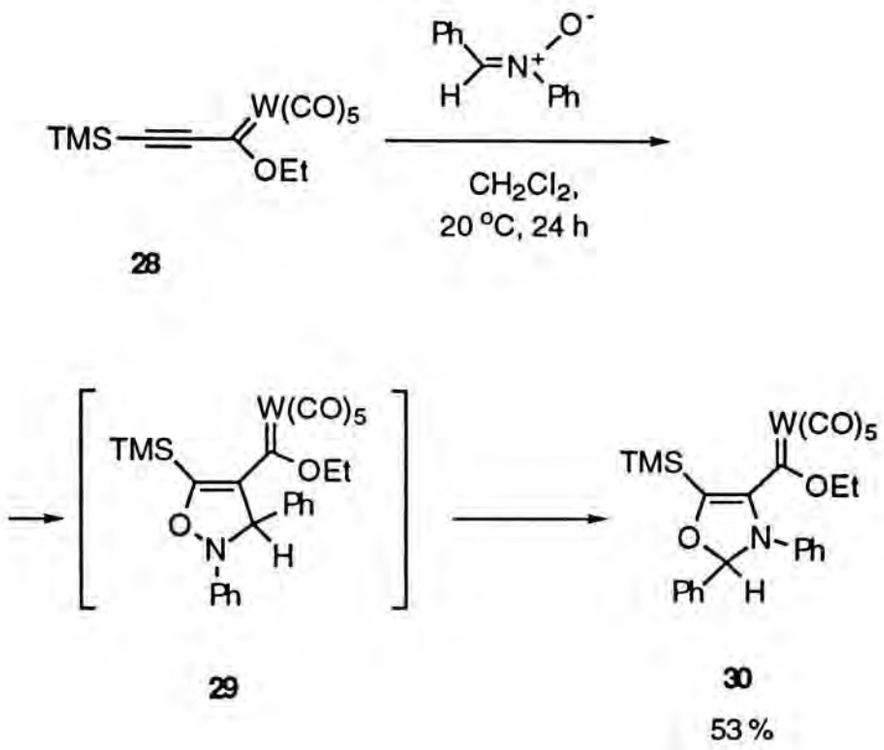
27

65 %

(6)

Scheme V

Another example of 1,3-dipole, *N*-phenyl nitrone, was found to undergo [3+2] cycloaddition with carbene complex **28** by Kalinin *et. al.* (Scheme VI),[15] however, the expected product **29** was proposed to appear transiently and then rearrange to **30** in 53 % yield for 1 day at 25 °C. Indeed, this rearrangement of organic isoxazolines to oxazolines takes place after prolonged heating in benzene.[16]



Scheme VI

However, Chan has found that the same 1,3-dipole but with different *N*-substitutent, α-phenyl *N-tert*-butyl nitrone (PBN) **35d** undergoes chemoselective and regioselective [3+2] cycloaddition with phenyl substituted carbene complexes to give essentially quantitative yields of 2,3-dihydroisoxazole carbene complexes (eq 10), without the isoxazoline-oxazoline rearrangement mentioned above, at room temperature accompanied by a great rate enhancement over the corresponding ester analogue.[16]

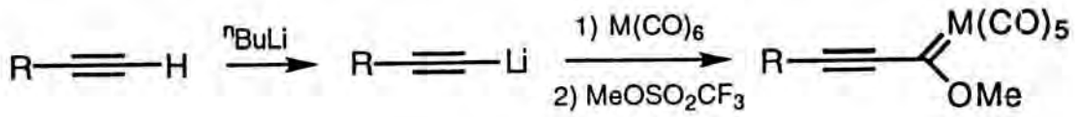
In the following section, we will first report on the [3+2] cycloaddition of alkynyl Fischer carbene complexes with *N*-alkyl nitrones. After that, kinetic studies of the reaction will be discussed.

II. RESULTS AND DISCUSSION

II-1. [3+2] Cycloaddition of Alkynyl Fischer Carbene Complexes with *N*-alkyl Nitrones

Preparation of Fischer Carbene Complexes. Alkynyl Fischer carbene complexes were prepared as described in the literatures (Eq 7).[14,17] The terminal acetylene was first lithiated by *n*-butyllithium, followed by nucleophilic attack at a carbonyl carbon of metal hexacarbonyl, and methylation was then achieved by the strong methylation agent, trifluoromethylsulfonate, to give the desired carbene complexes. For alkenyl carbene complexes, substituted alkenyl bromides were used as the starting materials instead.

Table I. Preparation of Carbene Complexes **31a-d**.



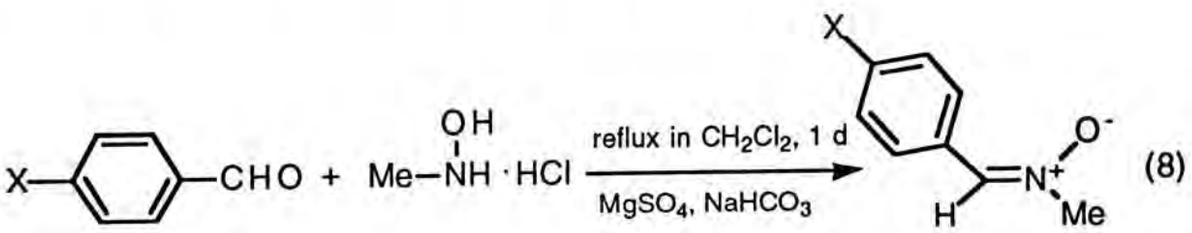
(7)

Complex	M	R	% yield (Lit.)
31a	Cr	Ph	43 (49)[39]
31b	W	Ph	41 (51)[39]
31c	Cr	*p*-MeC_6H_5	45
31d	W	*p*-MeC_6H_5	25

Preparation of Nitrones. *N*-alkyl nitrones were conveniently prepared by two reported methods. The first method employs the condensation of alkyl-hydroxylamine with aldehyde[18] and the second method takes advantage of the oxidation of secondary amines by hydrogen peroxide in the presence of catalytic amount of sodium tungstate.[19] A series of α-phenyl *N*-methyl **32a-h** (X-PMN) (Table II) and α-phenyl *N-tert*-butyl nitrone **35a-f** (X-PBN) (Table III) were prepared by the condensation of

aldehydes with the corresponding hydroxylamines in refluxing CH_2Cl_2 in a suspension of anhydrous $MgSO_4$ according to the procedure of Torssell and Zeuthen.[18] For the preparation of *N*-methyl nitrone, $NaHCO_3$ was added to neutralize the commerically avaliable methylhydroxylamine hydrochloride to generate MeNHOH. In the preparation of *N-tert*-butyl nitrone, the reaction required refluxing under nitrogen in order to avoid undesired aerobic oxidation of *N-tert*-butylhydroxylamine **34** (preparaed by reduction of 2-methyl-2-nitropropane **33** with aluminum amalgam)[20] to the nitroso compound. The yields of *N*-methyl nitrones **32** (73 to 90 %) were generally higher than those of *N-tert*-butyl nitrones **35** (47 to 90 %), likely due to less bulky methyl group in facilitating the condensation. Alternatively, the non-substituted *N-tert*-butyl nitrone **35d** and *N*-benzyl nitrone **36** (PBnN) were prepared by slow addition of aqueous hydrogen peroxide into a methanol solution of *tert*-butylbenzylamine and dibenzylamine respectively in the presence of sodium tungstate at 0 °C.[19]

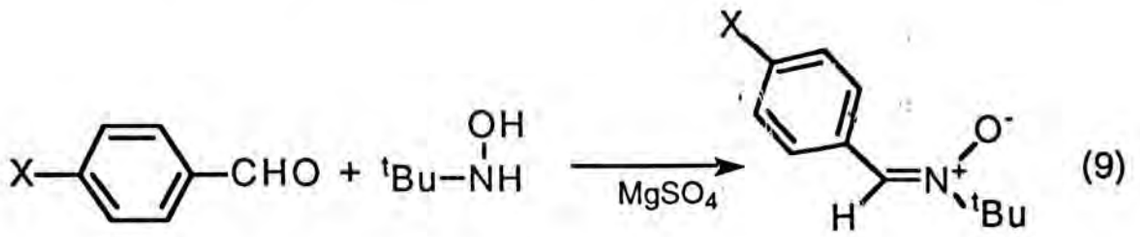
Table II. Preparation of Substituted *N*-methyl Nitrone **32a-h** (X-PMN).



X-PMN, **32a-h**

X-PMN	yield (%)
32a NMe_2-PMN	87
32b OMe-PMN	80
32c Me-PMN	87
32d H-PMN	85
32e Br-PMN	70
32f Cl-PMN	73
32g CN-PMN	90
32h NO_2-PMN	90

Table III. Preparation of Substituted *N-tert*-butyl Nitrone **35a-c, 35e-f** (X-PBN).



34 X-PBN, **35a-c, 35e-f**

X-PBN		solvent	reaction time (d)	reaction temp	yield (%)
35a	Me_2N-PBN	CH_2Cl_2	4	reflux	47
35b	MeO-PBN	CH_2ClCH_2Cl	1	reflux	63
35c	Me-PBN	CH_2Cl_2	1	reflux	90
35e	Br-PBN	CH_2Cl_2	6	r. t.	61
35f	Cl-PBN	CH_2Cl_2	1	reflux	75

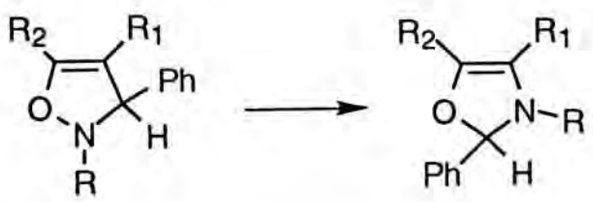
Cycloadditions of Carbene Complexes with Nitrones. When pyridine *N*-oxide was reacted with complex **31a**, instead of undergoing [3+2] cycloaddition at the carbon-carbon triple bond, undesired oxidative cleavage of chromium-carbon double bond was observed to give methyl 2-phenylethynyl carboxylate (**37**).[21] However, when a more reactive nitrone PBN **35d** was treated with carbene complexes of chromium **31a** and tungsten **31b**, it underwent chemoselective cycloadditions at the carbon-carbon triple bond to give the dihydroisoxazole carbene complexes **40d** and **41d** in excellent yields (Table VII, entry 4 & 16). Besides, the yield of the cycloadduct **40d** remained practically the same when **31a** was reacted with either 1 or 2 equiv of H-PBN **35d** (Table VII, entry 4 & 5). Double cycloaddition and oxidative cleavage were, therefore, insignificant.[21]

Besides, the cycloadditions were highly regioselective since only one regioisomer was observed and the regioselectivity was at least over 20 to 1 based on ^1H NMR analysis. The regiochemistry of the cycloadducts was secured by NOE experiments. Upon irradiation of the methoxy protons, NOE enhancements were

observed at the methine protons [% NOE: Cr complex **40d** = 2.0, W complex **41d** = 0.8]. Other carbene complex cycloadducts were therefore assigned to have the same regiochemistry.[21]

The above NOE experiment not only determined the regiochemistry of the *N*-*tert*-butyl cycloadduct **40d** but also ruled out the possibility of the isoxazoline-oxazoline rearrangement (Scheme VI). Cycloadduct **40d** had been heated at 40 °C in benezene-d_6 for 2 days, however, no obvious change of the NMR spectrum was observed. After that, the cycloadduct had been heated at elevated temperature of 80 °C for another 2 days. It was decomposed and no rearranged product was found. Indeed, the latter experimental conditions could change organic *N*-phenyl isoxazoline to oxazoline (Table IV, the last two entrys) readily.[16] For *N*-methyl isoxazoline, however, more drastic condition of higher temperature (160 °C) was needed (Table IV, the first entry). These results are consistent with the findings that the rearrangement occurs readily in the *N*-phenyl cycloadduct complex (Scheme VI) but not in the *N*-alkyl cycloadduct complexes **39-41**. Again, the reason of this rearrangement is not clearly known.

Table IV. Isoxazoline-Oxazoline Rearrangement.[16]



R	R_1	R_2	conditions
CH_3	CO_2CH_3	Ph	Isoxazoline heated in boiling mesitylene (160 °C)
Ph	CO_2CH_3	Ph	Obtained directly from cycloaddition reactions in boiling ethyl acetate (77 °C); no isoxazoline isolated.
Ph	H	CO_2CH_3	Obtained directly from cycloaddition reactions in boiling benzene (80 °C); no isoxazoline isolated.

The structure of *N*-methyl cycloadduct **39d** was determined by X-ray diffraction (Fig. 1), which further consolidated the fact that the *N*-alkyl cycloadduct would not undergo isoxazoline-oxazoline rearrangement at room temperature. The bond lengths and valence angles are listed in Table V and VI. The coordination sphere of the tungsten atom shows a distorted octahedral geometry with the W(1)-C(6) carbene bond distance of 2.198 (7) Å, which is longer than those in alkoxy carbene tungsten complexes [2.16 (1) Å, Orpen, Brammer, Allen, *et al*, 1989; 2.162 (6) Å, Fehlhammer, Riegger, Lotz, *et al*, 1993],[22] but significantly shorter than those in the analogous α,β-unsaturated carbene tungsten complex [2.250 (4) Å, Pipoh, Eldik and Henkel, 1993].[23] The W-CO bond in the *trans*-position relative to the carbene ligand [2.021 (9) Å] is somewhat shorter than those in the *cis*-position [2.053 (10) Å on average], since the carbene ligand is a weaker π-acceptor than CO and exerts a weaker trans-influence.[24] The carbonyl groups C(3)O(3) and C(4)O(4) were found to bend from the carbene ligand [the C(3)-W(1)-C(6) = 96.2 (3)^{o} and C(5)-W(1)-C(6) = 94.2 (3)^{o} are greater than 90^{o}]. This is due to the steric repulsions of C(3)O(3) group from methoxy group and of C(4)O(4) group from phenyl ring of the C(18)..C(23). The five-membered heterocycle composed of O(7), N(1), C(8), C(9) and C(10) is a planar ring with a mean deviation of 0.06 Å, and the dihedral angles between this plane and two substituted phenyl groups are 41.7 and 82.5^{o} respectively.

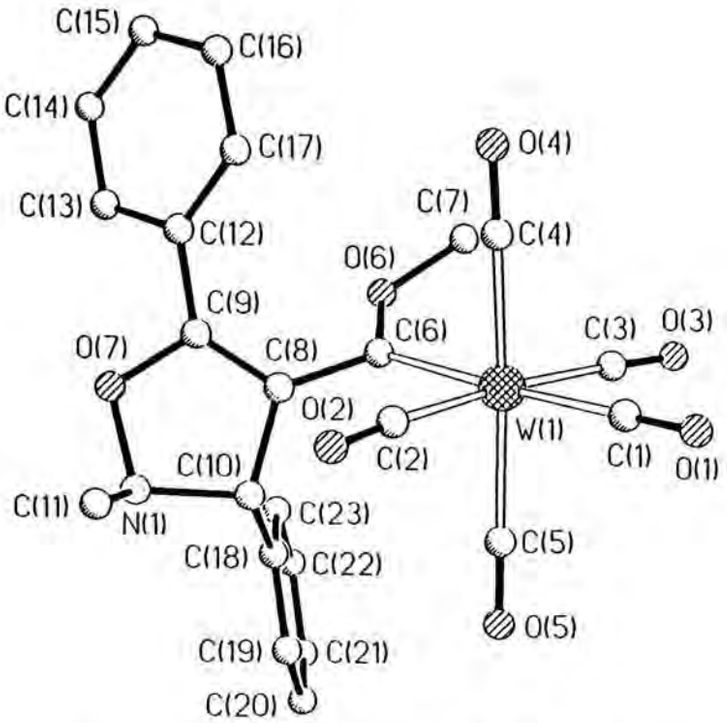


Figure 1. The Structure of PMN **39d**.

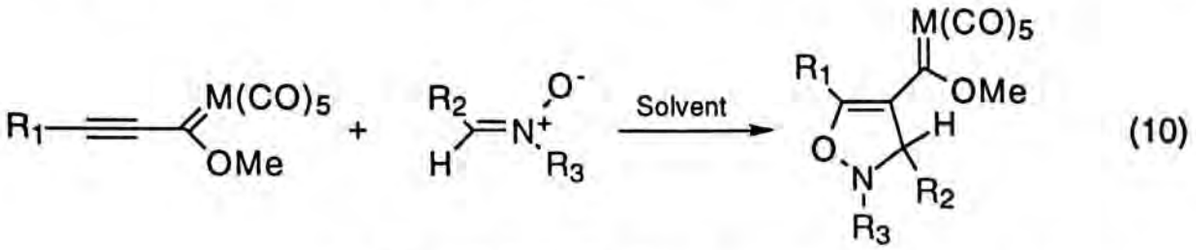
Table V. Bond Lengths of Cycloadduct **39d**.

Bond	d, Å	Bond	d, Å	Bond	d, Å
W(1)-C(1)	2.021 (9)	O(3)-C(3)	1.15 (1)	N(1)-C(11)	1.46 (2)
W(1)-C(2)	2.05 (1)	O(4)-C(4)	1.12 (1)	C(6)-C(8)	1.45 (1)
W(1)-C(3)	2.05 (1)	O(5)-C(5)	1.13 (1)	C(8)-C(9)	1.35 (1)
W(1)-C(4)	2.05 (1)	O(6)-C(6)	1.35 (1)	C(8)-C(10)	1.51(1)
W(1)-C(5)	2.06 (1)	O(6)-C(7)	1.45 (1)	C(9)-C(12)	1.48 (1)
W(1)-C(6)	2.198 (7)	O(7)-N(1)	1.47 (1)	C(10)-C(18)	1.52 (1)
O(1)-C(1)	1.14 (1)	O(7)-C(9)	1.350 (9)	C-C(Ph at C(9))	1.382 (17)
O(2)-C(2)	1.15 (1)	N(1)-C(10)	1.52 (1)	C-C(Ph at C(10))	1.380 (17)

Table VI. Valence Angles of Cycloadduct **39d**.

Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
C(1)-W(1)-C(2)	89.5 (4)	W(1)-C(4)-O(4)	179.4 (9)	C(8)-C(10)-C(18)	113.8 (7)
C(1)-W(1)-C(3)	85.1 (4)	W(1)-C(5)-O(5)	176.7 (8)	C(9)-C(12)-C(13)	119.3 (7)
C(2)-W(1)-C(3)	173.9 (4)	C(6)-O(6)-C(7)	123.3 (7)	C(9)-C(12)-C(17)	122.8 (8)
C(1)-W(1)-C(4)	90.6 (4)	N(1)-O(7)-C(9)	108.0 (6)	C(13)-C(12)-C(17)	117.8 (9)
C(2)-W(1)-C(4)	89.1 (4)	O(7)-N(1)-C(10)	105.0 (6)	C(12)-C(13)-C(14)	121.3 (9)
C(3)-W(1)-C(4)	93.9 (5)	O(7)-N(1)-C(11)	104.8 (8)	C(13)-C(14)-C(15)	120 (1)
C(1)-W(1)-C(5)	88.4 (4)	C(10)-N(1)-C(11)	112.7 (7)	C(14)-C(15)-C(16)	121 (1)
C(2)-W(1)-C(5)	85.9 (4)	W(1)-C(6)-O(6)	128.6 (5)	C(15)-C(16)-C(17)	120 (1)
C(3)-W(1)-C(5)	91.0 (5)	W(1)-C(6)-C(8)	124.5 (6)	C(12)-C(17)-C(16)	120.9 (9)
C(4)-W(1)-C(5)	174.9 (4)	O(6)-C(6)-C(8)	106.7 (6)	C(10)-C(18)-C(19)	119.7 (8)
C(1)-W(1)-C(6)	177.0 (4)	C(6)-C(8)-C(9)	127.0 (8)	C(10)-C(18)-C(23)	122.1 (9)
C(2)-W(1)-C(6)	89.3 (3)	C(6)-C(8)-C(10)	125.6 (8)	C(19)-C(18)-C(23)	118 (1)
C(3)-W(1)-C(6)	96.2 (3)	C(9)-C(8)-C(10)	107.3 (6)	C(18)-C(19)-C(20)	122 (1)
C(4)-W(1)-C(6)	86.7 (4)	O(7)-C(9)-C(8)	114.4 (8)	C(19)-C(20)-C(21)	119 (1)
C(5)-W(1)-C(6)	94.2 (3)	O(7)-C(9)-C(12)	113.7 (7)	C(20)-C(21)-C(22)	120 (1)
W(1)-C(1)-O(1)	177 (1)	C(8)-C(9)-C(12)	131.8 (7)	C(21)-C(22)-C(23)	121 (1)
W(1)-C(2)-O(2)	176.1 (8)	N(1)-C(10)-C(8)	103.4 (7)	C(18)-C(23)-C(22)	121 (1)
W(1)-C(3)-O(3)	175.8 (9)	N(1)-C(10)-C(18)	109.3 (6)		

Table VII. Cycloaddition of Alkynyl Fischer Carbene Complexes with Nitrones.



(10)

31a : R_1=Ph, M=Cr
31b : R_1=Ph, M=W
31c : R_1=*p*-Me-C_4H_6, M=Cr
31d : R_1=*p*-Me-C_4H_6, M=W
31e : R_1=TMS, M=Cr
31f : R_1=TMS, M=W

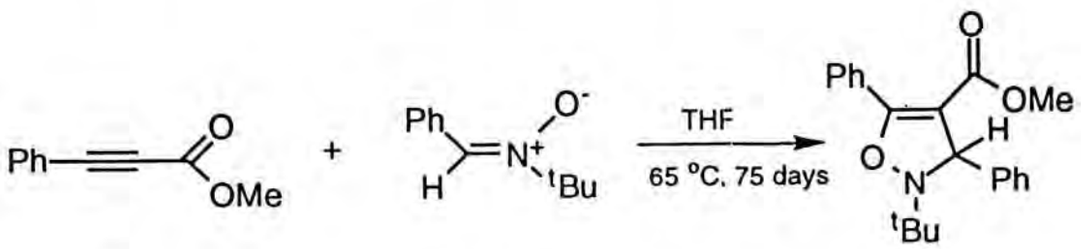
32 : R_2=*p*-X-C_4H_6, R_3=Me
35 : R_2=*p*-X-C_4H_6, R_3=^{t}Bu
36 : R_2=Ph, R_3=Bn

39 : R_1=Ph, M=W, R_2=*p*-X-C_4H_6, R_3=Me
40 : R_1=Ph, M=Cr, R_2=*p*-X-C_4H_6, R_3=^{t}Bu
41 : R_1=Ph, M=W, R_2=*p*-X-C_4H_6, R_3=^{t}Bu
42a : R_1=Ph, M=Cr, R_2=Ph, R_3=Bn
42b : R_1=Ph, M=W, R_2=Ph, R_3=Bn
43a : R_1=*p*-Me-C_4H_6, M=Cr, R_2=Ph, R_3=^{t}Bu
43b : R_1=*p*-Me-C_4H_6, M=W, R_2=Ph, R_3=^{t}Bu
44a : R_1=TMS, M=Cr, R_2=Ph, R_3=^{t}Bu
44b : R_1=TMS, M=W, R_2=Ph, R_3=^{t}Bu

entry	complex	nitrone	temp.	time	solvent	adduct	yield (%)
1	**31a**	**35a** NMe_2-PBN	r. t.	15 min	THF	**40a**	94
2	**31a**	**35b** MeO-PBN	r. t.	30 min	THF	**40b**	90
3	**31a**	**35c** Me-PBN	r. t.	40 min	THF	**40c**	98
4	**31a**	**35d** H-PBN	r. t.	3 h	THF	**40d**	95
5	**31a**	**35d** H-PBN (2 equiv)	r. t.	3 h	THF	**40d**	82
6	**31a**	**35d** H-PBN	r. t.	3 h	hexane	**40d**	92
7	**31a**	**35d** H-PBN	r. t.	1 h	acetone	**40d**	90
8	**31a**	**35d** H-PBN	r. t.	1 h	nitromethane	**40d**	87
9	**31a**	**35d** H-PBN	r. t.	1 h	acetonitrile	**40d**	88
10	**31a**	**35e** Br-PBN	r. t.	5 h	THF	**40e**	94
11	**31a**	**35f** Cl-PBN	r. t.	5 h	THF	**40f**	99
12	**31a**	**35h** NO_2-PBN	r. t.	4 d	THF	**40h**	42
13	**31b**	**35a** NMe_2-PBN	r. t.	5 min	THF	**41a**	92
14	**31b**	**35b** MeO-PBN	r. t.	15 min	THF	**41b**	95
15	**31b**	**35c** Me-PBN	r. t.	40 min	THF	**41c**	95
16	**31b**	**35d** H-PBN	r. t.	3 h	THF	**41d**	92
17	**31b**	**35e** Br-PBN	r. t.	5 h	THF	**41e**	99
18	**31b**	**35f** Cl-PBN	r. t.	5 h	THF	**41f**	96
19	**31c**	**35d** H-PBN	r. t.	3.5 h	THF	**43a**	88
20	**31d**	**35d** H-PBN	r. t.	1 h	THF	**43b**	95
21	**31e**	**35d** H-PBN	50 °C	20 h	THF	**44a**	26
22	**31f**	**35d** H-PBN	50 °C	40 h	THF	**44b**	35
23	**31b**	**32a** NMe_2-PMN	r. t.	5 min	THF	**39a**	50
24	**31b**	**32b** MeO-PMN	r. t.	5 min	THF	**39b**	65
25	**31b**	**32c** Me-PMN	r. t.	5 min	THF	**39c**	85
26	**31b**	**32d** H-PMN	r. t.	5 min	THF	**39d**	86
27	**31b**	**32e** Br-PMN	r. t.	5 min	THF	**39e**	97
28	**31b**	**32f** Cl-PMN	r. t.	5 min	THF	**39f**	75
29	**31b**	**32g** CN-PMN	r. t.	1 h	THF	**39g**	91
30	**31b**	**32h** NO_2-PMN	r. t.	5 h[a]	THF	**39h**	90
31	**31a**	**36** PBnN	r. t.	10 min	THF	**42a**	73
32	**31b**	**36** PBnN	r. t.	10 min	THF	**42b**	92

[a] NO_2-PMN was less soluble in THF compare with other PMN and higher dilution (7-fold dilution) was made to ensure it dissolve completely.

The cycloadditions of chromium carbene complex **31a** with PBN **35a-f** (Table VII, 1-4, 10-11) only took 15 min to 5 h to complete at room temperature and gave cycloadducts **40a-f** with excellent yields of above 90 %. The reaction of H-PBN **35d** with the closest organic analogue of complex **31a** or **31b**, methyl 2-phenylethynyl carboxylate (**37**) took 75 days at refluxing THF (65 °C) to give ester **38** in only 32 % together with unchanged ester (5 %) (eq 11).[25]

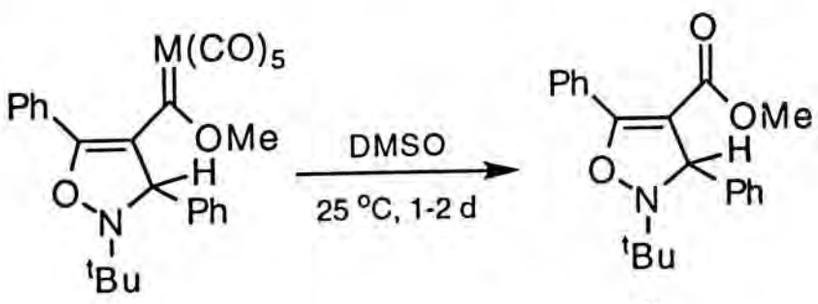


(11)

37 PBN, **35d** **38**

32 %

The rate enhancement of the metal pentacarbonyl moiety over the oxygen atom was estimated to be about 10^4. It was observed that the metal effect in the carbene complexes was insignificant. Both the yields and reaction times of the cycloadditions of tungsten carbene complex **31b** with PBN **35a-f** were similar to those of chromium complex **31a** (Table VII, entry 13-18). The cycloadduct complexes were easily oxidatively demetallated by DMSO or CAN to yield the ester **38** (eq 12).[21]



(12)

38

M=Cr, **40d** 94 %
M=W, **41d** 59 %

Apart from PBN, less sterically bulky nitrones such as *N*-benzyl (PBnN) **36** and *N*-methyl nitrone (PMN) **32a-h** were found to be much more reactive towards alkynyl carbene complexes. Complexes **31a** and **31b** reacted with PBnN **36** to give cycloadducts **42a** (73 %) and **42b** (92 %) within 10 min (Table VII, entry 31 & 32). Tungsten carbene complex **31b** reacted with PMN **32a-h** to give cycloadducts **39a-h** (Table VII, entry 23-30) with yields varying from 50 to 90 %. The reactions for all PMN were completed within 5 min except for CN-PMN **32g** and NO_2-PMN **32h** (Table VII, entry 29-30) as both of them have stronger electron withdrawing groups and their reactions with tungsten carbene complex **31b** took 1 h and 5 h to complete respectively. The cycloadducts **39a-h** with stronger electron withdrawing groups on the phenyl ring were found to be relatively stable although they decomposed slowly even when stored at -20 °C for about 1 month. The reaction time of *N*-methyl nitrones with carbene complexes were obviously shorter than that of *N-tert*-butyl nitrones. The reactivity of *N*-alkyl nitrones towards carbene complexes was in the following order (Table VII, entry 26, 32, 16): *N*-Me > *N*-Bn > *N*-^{t}Bu, since, presumably, the more steric crowding in the transition state decreases the rate of reaction. However, chromium carbene complex **31a** reacted with PMN **32d** to give thermally labile cycloadducts. At first, monitored by TLC, the reaction showed a new orange-red spot which turned black in air within several minutes. In order to examine if the transient product was the desired cycloadduct, the reaction was then carried out under nitrogen in a NMR tube in acetone-d_6 and monitored immediately at room temperature. A characteristic peak of methine proton of cycloadduct at δ 5.5 ppm was observed but disappeared after 3 min, which may be probably due to the formation of the unstable desired cycloadduct. The above results showed *N*-methyl tungsten cycloadduct was more stable than chromium cycloadducts presumably owing to the stronger metal carbon double bond.[26]

To gain a better understanding of the cycloaddition reaction, the substituent effect on nitrones was investigated. When carbene complex **31a** (or **31b**) was treated

with *para*-substituted PBN **35a-f**, the more electron donating substituent in the nitrone, NMe_2-PBN **35a**, reacted with carbene complex **31a** within 15 min (Table VII, entry 1). However, for Cl-PBN **35f** (Table VII, entry 11), it took about 5 h to complete the reaction. The above results concluded that the rate of reaction increased as the electron donating ability of the *para*-substitutent in *N-tert*-butyl nitrone **35a-f** increased.

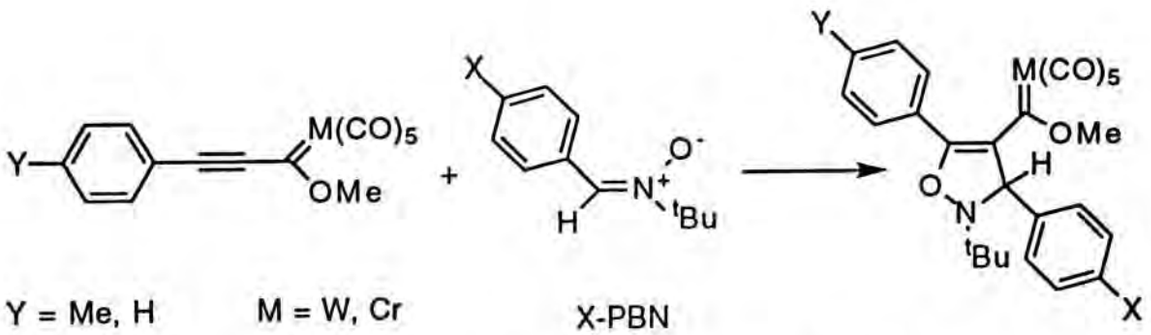
Frontier Molecular Orbital (FMO) theory serves to rationalize the reactivity and regioselectivity of cycloaddition reactions. Our results have indicated that the rate of cycloaddition of carbene complex with *N-tert*-butyl nitrones increases as the electron donating ability of the *para*-substitutent in *N-tert*-butyl nitrone increases. The reaction is likely due to the interaction between the LUMO of carbene complex and the HOMO of nitrone. For electron rich nitrone, higher HOMO energy level is expected and hence smaller HOMO-LUMO energy gap is resulted, consequently, the rate of reaction is increased.

In comparison with chromium carbene complex **31a**, *para*-methyl substituted chromium carbene complex **31c** is likely to have a higher LUMO energy level and is thus less reactive (3.5 h) (Table VII, entry 19). However, in the experiment, the rate was not significantly different from the non-substituted carbene complex **31a** and **31b** (3 h) (Table VII, entry 4 & 16).

In order to gain mechanistic insights of the cycloaddition, carbene complex **31a** was treated with H-PBN **35d** in five different solvents (Table VII, entry 4, 6-9). The reaction rates were 3-fold faster for reactions in the solvents with higher dielectric constants: acetone, acetonitrile and nitromethane than in THF and hexane. The small solvent effect indicated that the reaction might be a concerted one,[12] which will be further discussed in the following section.

II-2. Kinetic Studies of the [3+2] Cycloaddition

The α,β-unsaturated carbene complexes exhibit an impressive synthetic potential since they can either react as ester analogues due to the isolobal relationship[27] or participate in reactions not related to ester chemistry.[28] These reactions include the well-know Dotz reaction and show a number of advantages such as high regio- and stereoselectivity, large rate enhancement, and easy removal of the pentacarbonylmetal moiety. Although these complexes are of significant interest, kinetic studies have rarely been investigated. It is our objective to gain insights into the intimate nature of the cycloaddition mechanism. Besides, theoretical calculations of Fischer carbene complex and nitrones were also attempted to account for the reactivity and regioselectivity of the cycloaddition.



(13)

Y = Me, H M = W, Cr X-PBN

X = NMe_2, MeO, Me, H, Br, Cl, NO_2

The *N-tert*-butyl cycloadducts (**40d**, **41a-f** & **43b**) formed in the cycloaddition of carbene complexes with various substituted PBN (reaction 13) were isolated and fully characterized. Reaction 13 was accompanied by characteristic changes in the MLCT bands, as indicated in Figure 2. The reactions exhibited clean isobestic points for at least 3 half-lives. Generally, typical experimental conditions were [complex] = 6 x 10^{-5} M (unless otherwise specified, complex **31b** was used) and an at least tenfold excess of nitrone was used in order to establish pseduo-first-order conditions.

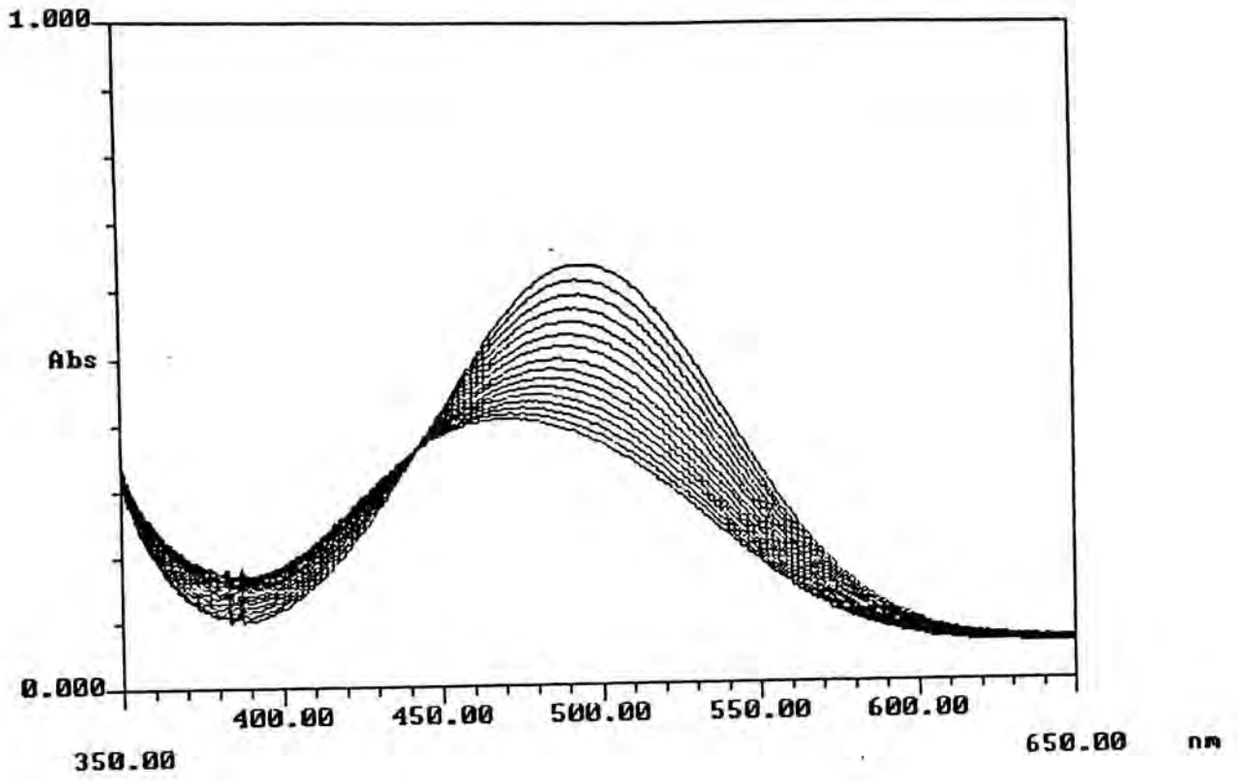


Figure 2. Repetitive Scan Spectra Recorded for the [3+2] Cycloaddition Reactions. Experimental Condition: [complex **36a**] = 5 x 10^{-5} M; T = 25 °C.

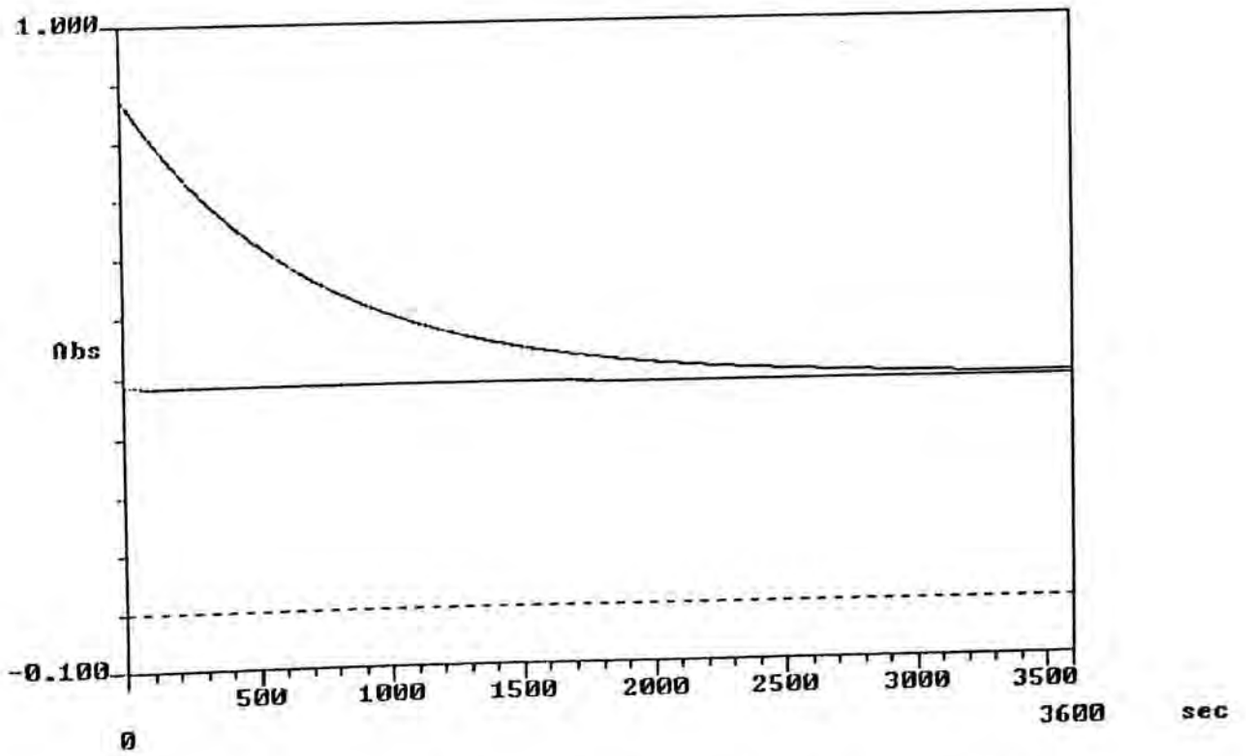


Figure 3. Time Scan for Reaction 13 (**31b** + PBN in hexane at 15.2 °C).

Kinetic measurements were performed at wavelengths where maximum absorbance changes λ_{max} occurred (λ_{max} for chromium carbene complex **39a** = 502 nm, while λ_{max} for tungsten complexes **31b** & **31d** = 486 nm). Time scan was then carried out at the specified wavelength λ_{max} for at least 3-half lives (Figure 3). Then the collected kinetic data were treated with Guggenheim's method (Appendix I).[29] By plotting ln $(A-A_{t+\Delta})$ *vs* t (where A is absorbance at time t, $A_{t+\Delta}$ is the absorbance at time $t+\Delta$, and Δ is a period two to three times as great as the half-life period of the reaction), a linear pseduo-first-order plot with slope equal to k_{obs} is obtained (Figure 4). Rate constants are summarized in Table VIII, which includes values for activation parameters determined by the temperature dependence of reactivities.

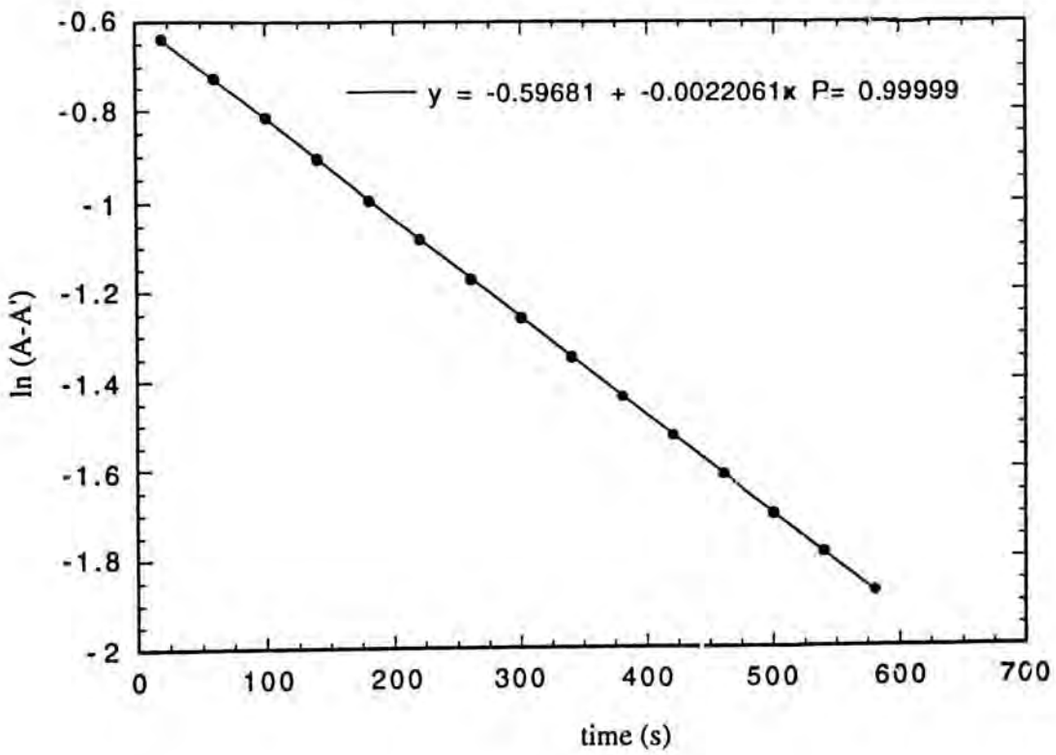
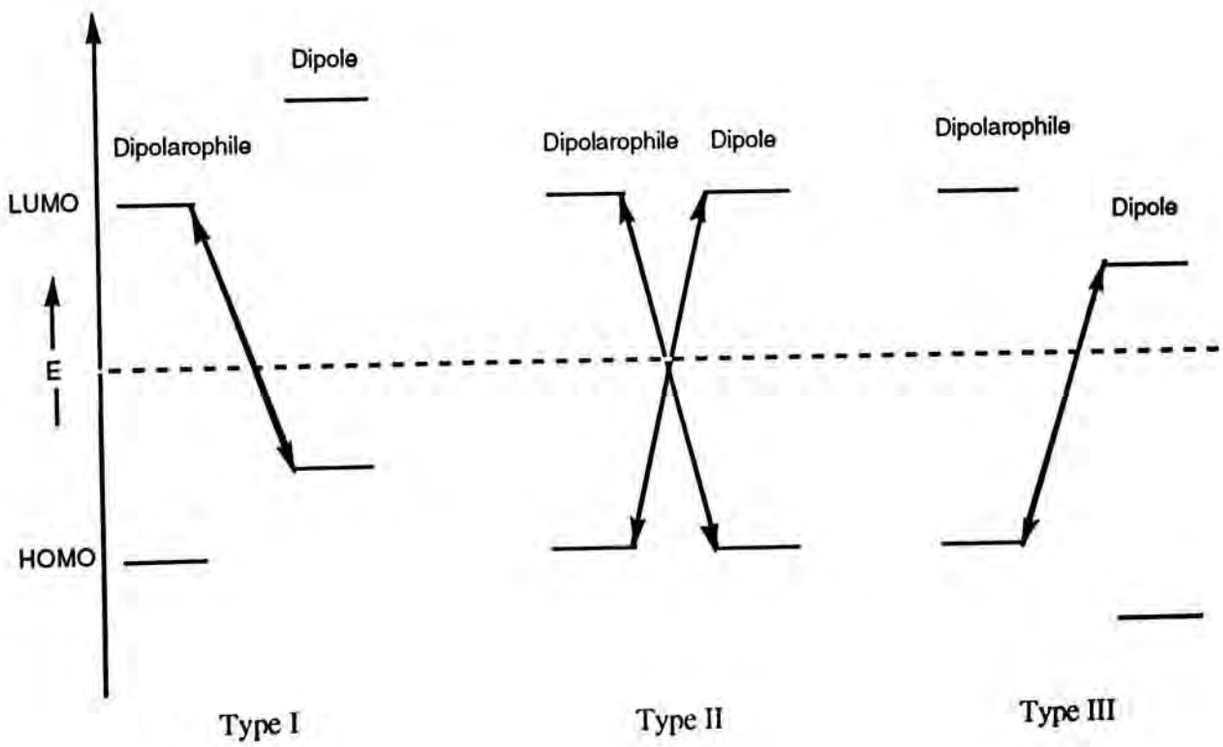


Figure 4. Pseudo-First-Order Plot of Reaction 13 of **31b** + PBN in Acetone at 34.2 °C.

Table VIII. Rate Constants and Activation Parameters of Reaction 13.

carbene complex	X-PBN	temp (°C)	solvent	k (10^{-4} $M^{-1}S^{-1}$)	$\Delta H^{\ddagger}$ ($kJmol^{-1}$)	$\Delta S^{\ddagger}$ ($Jmol^{-1}K^{-1}$)	$\Delta G^{\ddagger}_{298}$ ($kJmol^{-1}$)
31b	Me_2N	14.2 24.7 34.2 43.4	THF	93700 137000 154000 231000	19.5	-158.2	66.6
	MeO	14.8 24.7 34.7 44.2		6340 10100 14200 20100	26.9	-154.7	73.0
	Me	14.7 24.7 34.7 44.2		2480 4370 6340 9700	31.9	-145.1	75.1
	H	14.7 24.7 34.9 44.2		1370 2270 3640 5030	31.2	-152.5	76.6
	Br	15.3 24.7 34.0 43.7		390 673 960 1320	30.0	-167.3	79.9
	Cl	15.1 24.7 34.0 43.5		392 682 969 1420	31.5	-161.8	79.7
	NO_2	15.0 24.7 33.8 43.5		34 57 88 123	33.9	-174.3	85.8
	H	15.2 24.7 33.9 43.5	Hexane	1180 1810 2660 4040	30.4	-157.1	77.2
	H	15.2 24.7 34.2 43.4	Acetone	2210 3510 5380 7930	31.8	-146.8	75.5
	H	15.3 24.7 34.0 43.7	Acetonitrile	1880 3080 4460 7040	32.3	-146.5	76.0
31a	H	15.1 24.7 34.0 43.7	THF	499 770 1220 1870	32.8	-156.0	79.3
31d	H	15.2 24.8 33.8 43.2	THF	726 1180 1770 2570	31.8	-156.1	78.3

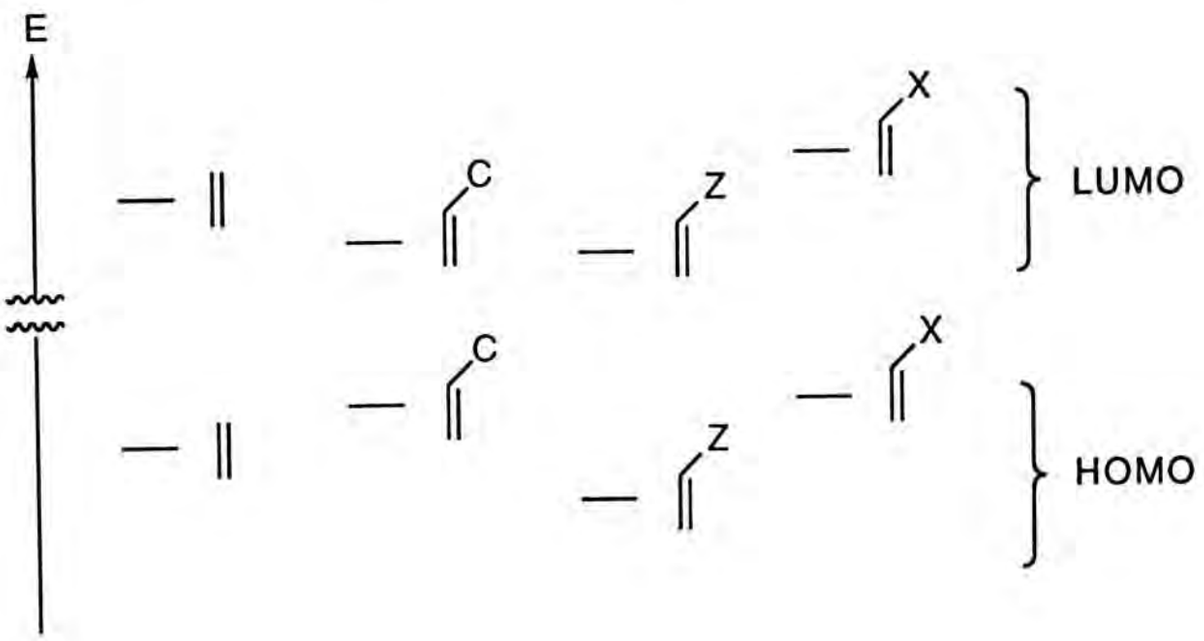
Before discussing the kinetic data, we will first spend some time on Frontier Molecular Orbital (FMO) theory, which has been applied to nitrone cycloadditions with impressive results in rationalizing both reactivity and regiochemical questions.[12] Cycloaddition processes have been classified into three types by Sustmann (Scheme VII).[30] The first one (Type I) involves a dominant interaction between the highest occupied molecular orbital (HOMO) of a dipole and the lowest unoccupied molecular orbital (LUMO) of a dipolarophile. Most of the Diels-Alder reactions fall into this classification. The second (Type III) is the reverse case of Type I, it involves a dominant HOMO (dipolarophile) - LUMO (dipole) interaction. The ozonization of the alkenes is one of the examples of Type III.[30] The last one (Type II) involves both HOMO (dipolarophile) - LUMO (dipole) and HOMO (dipole) - LUMO (dipolarophile) interactions, none of them is in dominant and hence the regioselectivity is expected to be poor.



Scheme VII. Frontier Molecular Orbital Classification of Cycloaddition Reaction.

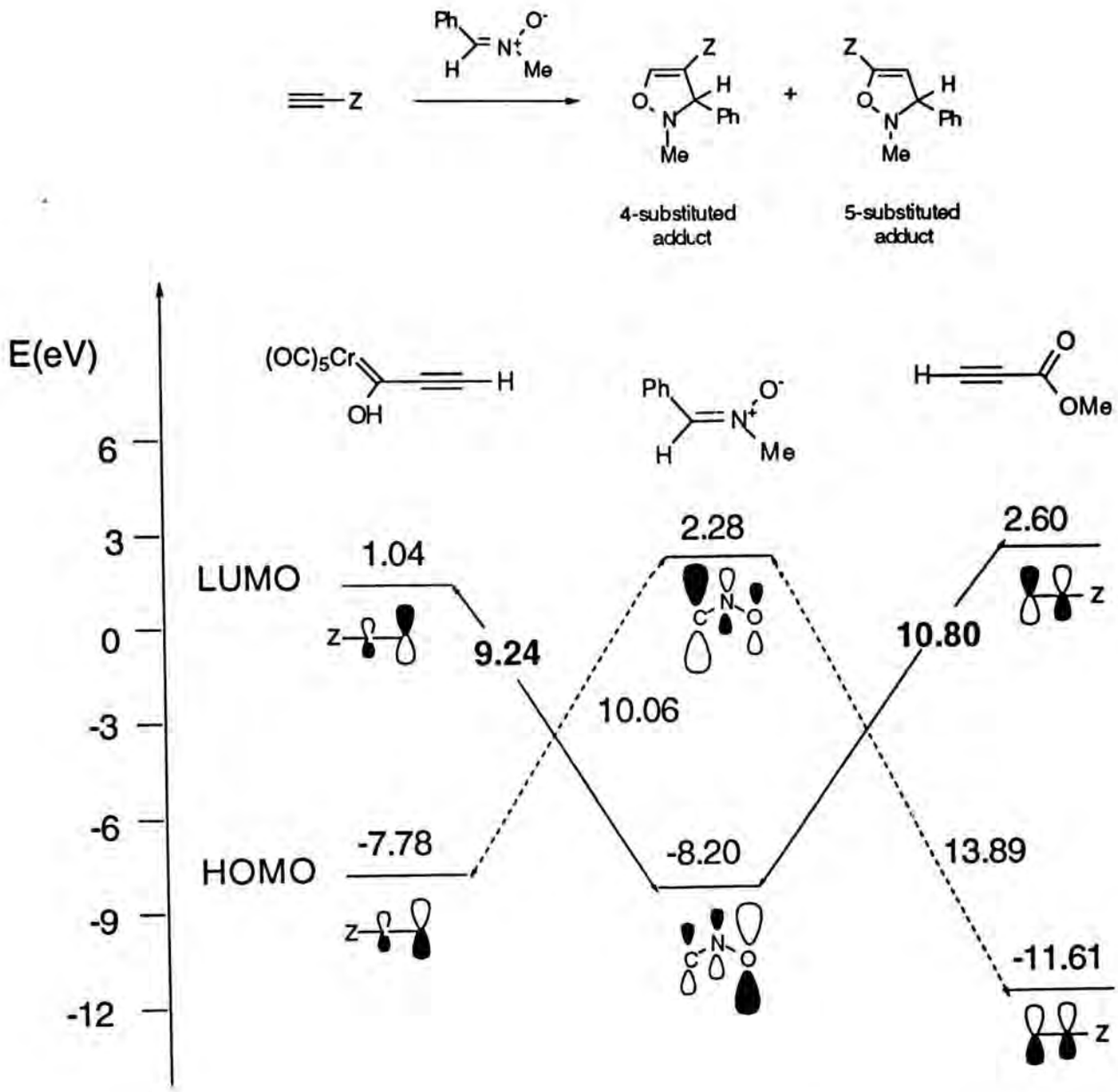
The FMO energies may be obtained empirically from the value of ionization potential (IP) to determine the HOMO energy, while the LUMO energy may be obtained from electron affinity (EA) data and may be derived from the HOMO energy (IP) with the approximate relationship EA = IP - $\Delta E(\pi\pi^*)$ - 4.5 eV.[31]

FMO energies varied due to the effects of substitutents may be estimated in an easy, non-mathematical way. For extra conjugation (C-), it raises the energy of the HOMO and lowers the energy of the LUMO; for an electron-withdrawing group (Z-), it lowers both the energies of HOMO and LUMO; for an electron-donating group (X-), it raises both the energies of HOMO and LUMO (Scheme VIII).[32]



Scheme VIII. Energies of the Frontier Orbitals of Dienophiles.

Scheme IX demonstrates the result of theoretical calculations[33] of the three given compounds and the cycloaddition processes of the chromium carbene complex and its organic ester analogue with the *N*-methyl nitrone (PMN). Both of the dipolarophiles adapt their LUMOs to interact with HOMO of PMN. The energy gap between the carbene complex and PMN is 9.24 eV, while that between the organic ester



Scheme IX. Frontier Orbital Energies and Energy Relationships between the Three Compounds.

and PMN is 10.84 eV. The energy gap for carbene complex is 1.60 eV (equivalent to 154 $kJmol^{-1}$) smaller than that for the organic ester analogue. The smaller energy gap of cycloaddition of carbene complex with PMN is a piece of evidence to account for its rate enhancement over the organic ester analogue. Besides, the LUMO (dipolarophile) - HOMO (dipole) interaction strongly favors the formation of the 4-substituted adduct, while LUMO (dipole) - HOMO (dipolarophile) interaction only weakly favors the formation of the 5-substituted adduct. Cycloaddition of methyl propiolate and nitrone involves LUMO (ester) - HOMO (nitone) interaction dominantly,

with the regioselectivity of 4-substituted adduct : 5-substituted adduct ≈ 1 : 1 (LUMO coefficient at terminal carbon is slightly larger than that at the adjacent one). The regioselectivity is comparable with the experimental result (5-substituted : 4-substituted = 42 : 58).[34]

The HOMO and LUMO energies[36] of substituted PMNs were calculated by *ab initio* method with basic set 3-21G using Gaussian 90 program[35] on IBM-RS6000-G90RevJ (Table IX). The HOMO energies of PMNs span from -7.821 to -8.514 eV. The HOMO energy of dimethyl amino group shows a deviation from the linear correlation of Hammett constants clearly, however, others indicate that the larger the electron donating ability, the higher the HOMO energies, and the energy gap between the carbene complex and PMN is then enlarged. So, it is expected that the electron rich nitrones accelerate the cycloaddition. However, this trend is not obvious for the cycloaddition of PMN. The reaction time is so short (5 min) that whatever the substitutent is (Table VII, entry 23-28), the rates are not significantly different. Kinetic studies of cycloaddition of tungsten carbene complex **31b** with PMN were not straight forward since the reaction was not clean enough to observe any isobestic point, the reason of which was probably the fast decomposition of the thermal labile cycloadduct. In fact, we have shown in Part II-1 that the tungsten *N*-methyl cycloadducts cannot stay long even in a freezer, while chromium *N*-methyl cycloadducts only appears transiently in the reaction mixtures. In view of this, we have selected *N-tert*-butyl nitrone cycloaddition as our kinetic study system.

Table IX. HOMO and LUMO Energies of PMN,[36] Calculated by *ab initio* Method (Basic Set: 3-21G) using Gaussian 90 Program.[35]

X-PMN	σ_p^o [a]	σ_p^+ [a]	HOMO (eV)	LUMO (eV)
MeO	-0.12	-0.78	-7.821	2.505
Me	-0.14	-0.3	-8.025	2.360
Me_2N	-0.32	-1.7	-8.073	2.339
H	0	0	-8.198	2.275
Br	0.26	0.15	-8.347	1.968
Cl	0.34	0.11	-8.514	1.883

[a]From reference 37.

Determination of the Rate Equation

The isolation experiment on reaction 13 with the rate equation $v = k$ [complex]^m [nitrone]^n was first performed to determine the order with respect to complex, by setting [nitrone]$_{initial}$ >>> [complex]$_{initial}$, $v = k_{obs}$ [complex]^m, where $k_{obs} = k$ [nitrone]$_{initial}$, thus establishing pseudo-mth-order kinetics. By following the decrease of absorbance of carbene complex and plotting ln (A-A') against time, a linear pseudo-first-order plot was yielded (Figure 4) and hence the reaction was first order with respect to complex. It was not analytically convenient to use the isolation technique to determine the order with respect to nitrone, because it was easier to observe the carbene complex spectrophotometrically than to follow the loss of nitrone. Therefore, the preceding experiment was repeated at several nitrone concentrations and from the pseudo-first-orde plots the pseudo-first-order rate constants were determined. These data are shown in Table X. The rate equation is now $v = k_{obs}$ [complex], where we anticipate $k_{obs} = k$ [nitrone]^n. The third column of Table X lists the quotient k_{obs}/[nitrone]$_{initial}$, whose constancy shows that $n = 1$. Therefore, the rate equation may be written as:

$$v = k \text{ [complex] [nitrone]}$$

Table X. Determination of Reaction Order from Pseudo-First-Order Rate Constants.[a]

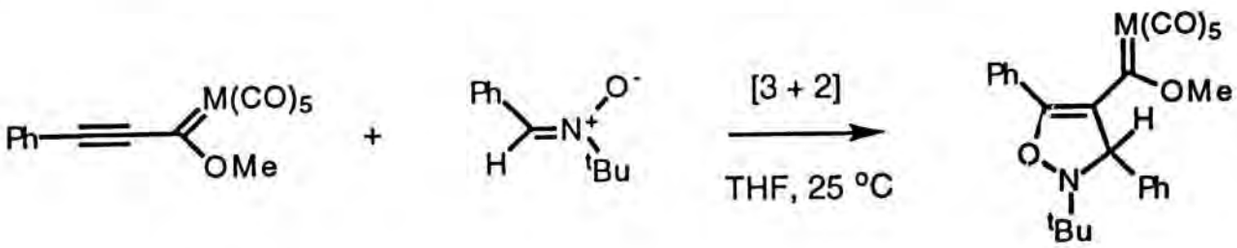
[nitrone]$_{initial}$ (10^{-4} M)	k_{obs} (10^{-4} s^{-1})	k (M^{-1} s^{-1})
6.3	1.33	0.21
12	2.86	0.24
30	6.93	0.23
60	13.7	0.23

[a]For reaction 13 with [complex]$_{initial}$ = 6.0 x 10^{-5} M in THF at 24.7 °C.

Metal Effect on Carbene Complex:

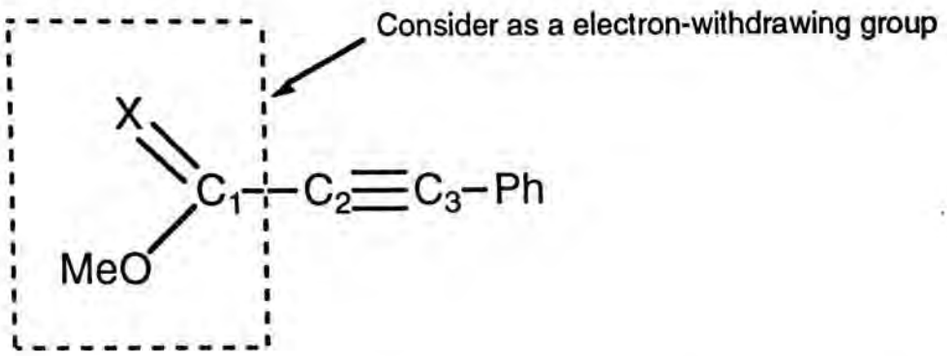
The data in Table XI demonstrate that the reactivity of carbene complexes **31b** is 2.9 times faster than **31a** at 25 °C. From the ^{13}C chemical shifts (Table XII),[38] the order of the downfield shift at C_2 position(or electron withdrawing ability) is in the order: **31b** (98 ppm) > **31a** (92 ppm) > **34** (82 ppm). From FMO consideration, **31b** has lowest LUMO energy and smaller energy gap of LUMO (complex) - HOMO (nitrone), hence the rate is the fastest among the three compounds. This metal effect is also observed in other cycloaddition systems, for example, the [2+2] cycloaddition. Scheme X demonstrates that the tungsten carbene complex is faster than the chromium by 1.6 times.[11] This effect of the metal on the reactivity is also known and described for substitution reactions of metal carbonyl complexes of group VIb.[39]

Table XI. Rate Constants of the Two Metal Carbene Complexes.



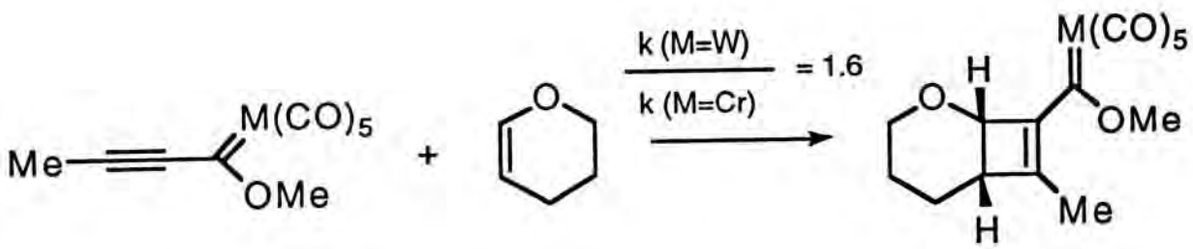
complex	M	k (10^{-3} M^{-1} S^{-1})	k_{rel}
31a	Cr	77	1
31b	W	227	2.9

Table XII. The ^{13}C Chemical Shifts of the Three Compounds.[38]



complex	X	$\delta(C_1)$	$\delta(C_2)$ (ppm)	$\delta(C_3)$
34	O	153.2	81.8	87.9
31a	$Cr(CO)_5$	315.0	92	135.7
31b	$W(CO)_5$	288.0	98	*a*

[a]Not determined.

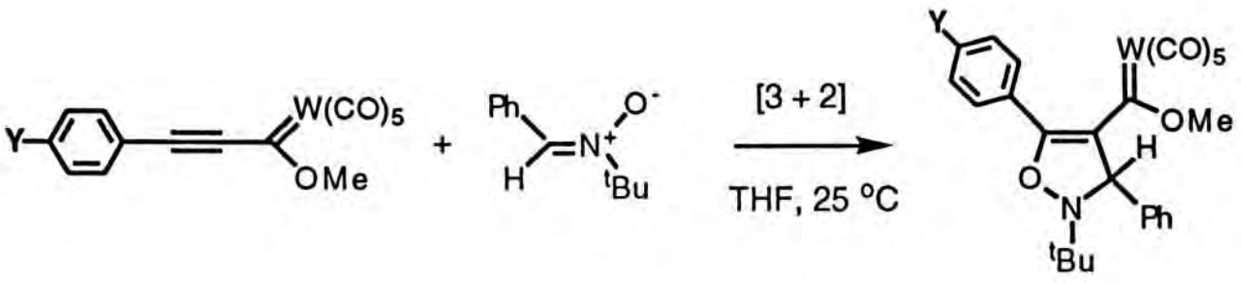


Scheme X. The Metal Effect on [2+2] Cycloaddition.[11]

Substitutent Effect on Carbene Complex

The substitutent effect on carbene complex is not fully investigated. The methyl substituted carbene complex **31d** is found two times slower than the non-substituted one **31b** (Table XIII). This is due to the electron donating group (methyl group) in raising the LUMO energy level of the complex to enlarge energy gap of cycloaddition.

Table XIII. The Substituted Effect on Carbene Complex.



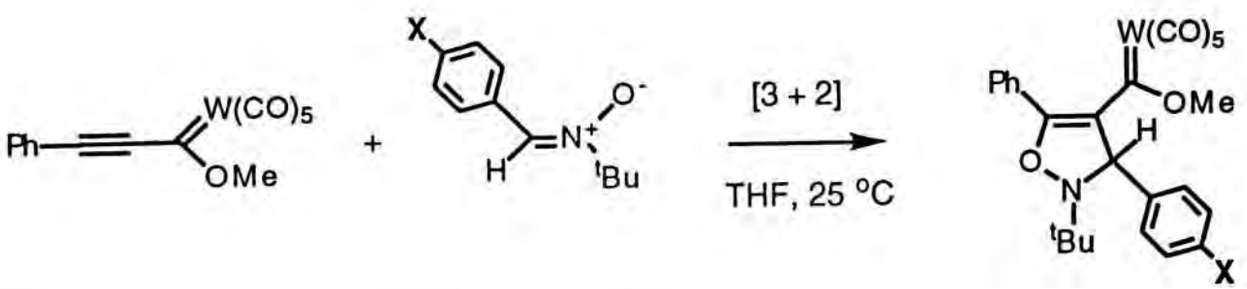
complex	Y	σ_p^o [a]	σ_p^+ [a]	k (10^{-3} $M^{-1}S^{-1}$)	k_{rel}
31d	Me	-0.14	-0.3	118	1
31b	H	0	0	227	1.9

[a]From reference 37.

Substitutent Effect on Nitrone

The data shown in Table XIV demonstrate that the reaction is accelerated by the electron rich nitrone. This observation is consistent with the FMO diagram shown in Scheme IX that the electron rich nitrone raises the HOMO energy level, decreases the energy gap of the cycloaddition and consequently accelerates the reaction. A Hammett linear free energy treatment of the data (Table XVI) gives a ρ value, a measure of the sensitivity of the reaction rate towards substitutent changes, of -3.15 (Figure 5, r = 0.9191) using σ_p^o constants and -1.19 (Figure 6, r = 0.9839) using σ_p^+ constant, It is found that the correlation coefficient for σ_p^+ plot is larger than that of σ_p^o plot. It implies that the reaction may involve an enhanced resonance transition state. The magnitude of ρ^+ obtained from the Hammett plot (-1.19) is quite different from those observed for typical ionic processes (-3.3 to -4.3)[40] and is comparable with other concerted [3+2] cycloaddition.[41]

Table XIV. The Substitutent Effect on Nitrone.



nitrone	X	σ_p^o [a]	σ_p^+ [a]	k (10^{-3} M^{-1} s^{-1})
35a	Me_2N	-0.32	-1.7	13700
35b	MeO	-0.12	-0.78	1010
35c	Me	-0.14	-0.3	440
35d	H	0	0	230
35e	Br	0.26	0.15	67
35f	Cl	0.34	0.11	68
35g	NO_2	0.81	-	6

[a]From reference 37.

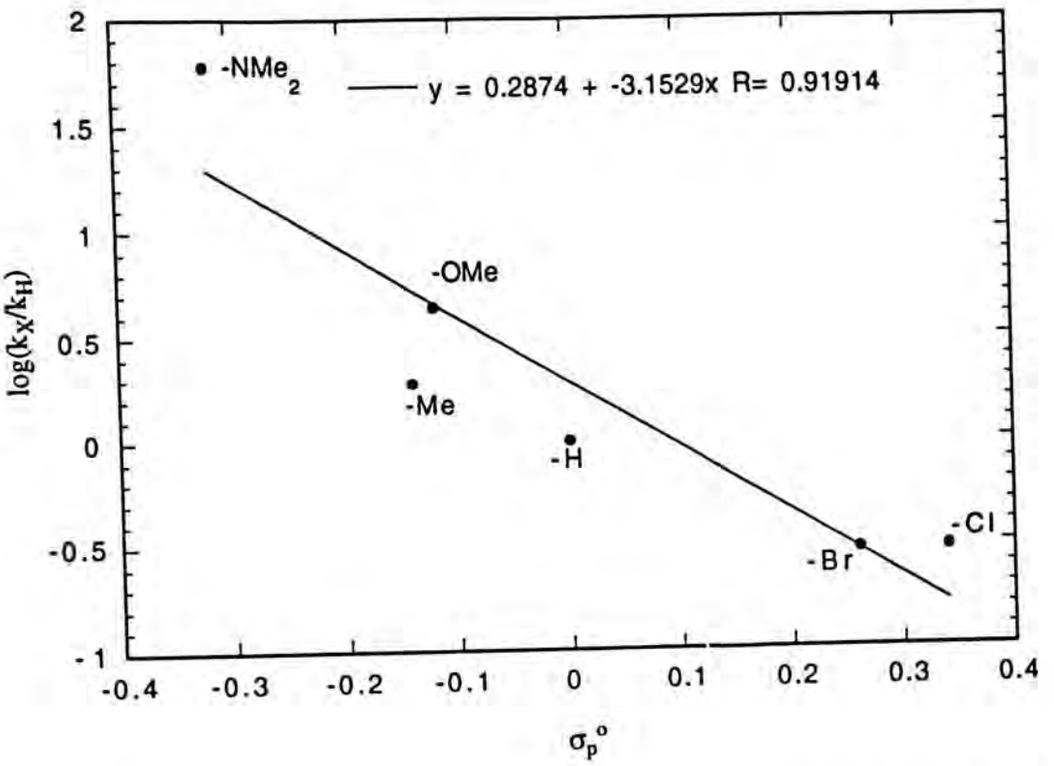


Figure 5. Plot of Log (k_X/k_H) verse σ_p^o for Reaction 13 of Substituted PBNs.

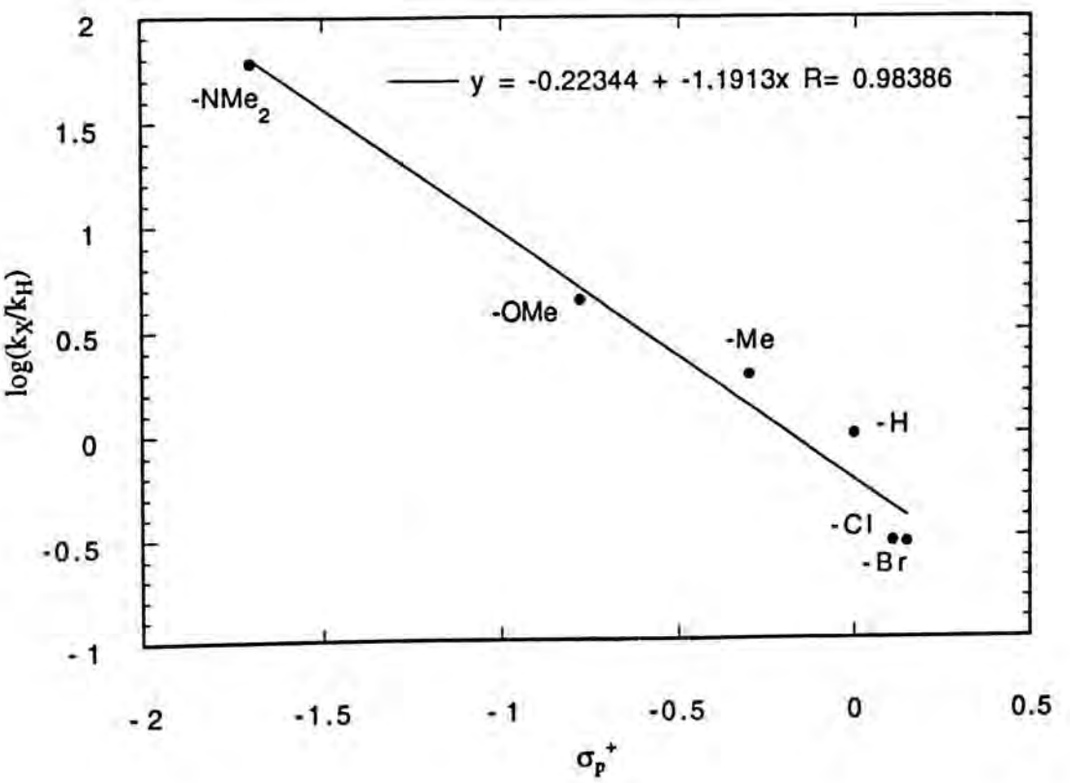


Figure 6. Plot of Log (k_X/k_H) verse σ_p^+ for Reaction 13 of Substituted PBNs.

Temperature Dependence

In the following equation, it can be seen that a plot of ln (k/T) against 1/T has a slope of $-\Delta H^{\ddagger}/R$ and a y-intercept of ln (**k**/h) + $\Delta S^{\ddagger}/R$. Such a graph is called an Eyring plot (Figure 7) which yields the activation parameters.

$$\ln (k/T) = -\Delta H^{\ddagger}/(RT) + \ln (\mathbf{k}/h) + \Delta S^{\ddagger}/R$$

where **k** is the Boltzmann constant;

R is the Gas constant;

h is the Planck's constant.

The small values of $\Delta H^{\ddagger}$ (between 19 and 34 kJmol^{-1}) and large negative activation entropies $\Delta S^{\ddagger}$ (-146 to -174 JK^{-1}mol^{-1}) (Table XV) indicate the bond formation between the carbene complex and nitrone through a highly structured transition state.

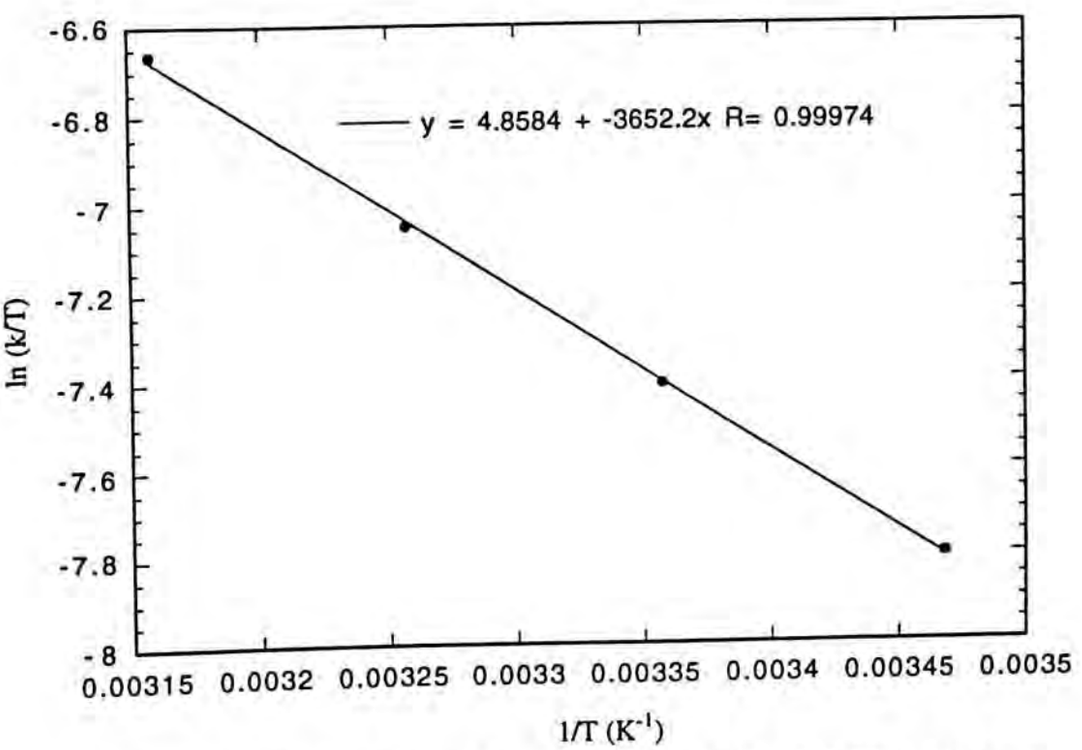


Figure 7. Eyring Plot of Reaction 13 of **31b** + PBN in Hexane.

In principle, cycloaddition reaction can be classified as a two-step process via the formation of a zwitterionic intermediate or a one-step process involving a transition state either with considerable dipole formation (concerted but non-synchronous one-step mechanism) or without significant charge separation (synchronous one step mechanism). It is well-known that the determination of reaction rates and activation parameters in various solvents is one of the useful methods to distinguish between different reaction mechanisms.

Table XV. Summary of Activation Parameters of Reaction 13.

carbene complex	X-PBN	solvent	$\Delta H^{\ddagger}$ ($kJmol^{-1}$)	$\Delta S^{\ddagger}$ ($Jmol^{-1}K^{-1}$)	$\Delta G^{\ddagger}_{298}$ ($kJmol^{-1}$)
31b	Me_2N	THF	19.5	-158.2	66.6
	MeO		26.9	-154.7	73.0
	Me		31.9	-145.1	75.1
	H		31.2	-152.5	76.6
	Br		30.0	-167.3	79.9
	Cl		31.5	-161.8	79.7
	NO_2		33.9	-174.3	85.8
	H	Hexane	30.4	-157.1	77.2
	H	Acetone	31.8	-146.8	75.5
	H	Acetonitrile	32.3	-146.5	76.0
31a	H	THF	32.8	-156.0	79.3
31d	H	THF	31.8	-156.1	78.3

Solvent Effect

Reaction 13 was examined in several selected solvents covering a large polarity range (Table XVI). However, the observed rate constants do not exhibit a significant solvent dependence, at the most a factor of 2. This indicates that there is no large charge separation in the activated complex than in the reactants and the reaction probably goes through one step, concerted pathway.

Table XVI. Rate Constants at the Four Different Solvents.

Solvent	ε [a]	D_n [a]	E_T [a]	k (10^{-2} $M^{-1}S^{-1}$)	Rate ratio
MeCN	37.5	14.1	46.0	31	1.7
Acetone	20.7	17.0	42.2	35	1.9
THF	7.6	20.0	37.4	23	1.3
Hexane	1.9	-	30.9	18	1

[a] From reference 41b.

III. CONCLUSION

Alkynyl Fischer carbene complexes have been demonstrated to undergo chemoselective and regioselective [3+2] cycloaddition with *N*-alkyl nitrone to give 2,3-dihydroisoxazole carbene complexes in excellent yields with rate enhancement of 10^4 over alkynyl organic ester observed. The reaction is found to be controlled by HOMO (nitrone) - LUMO (carbene complex) interaction both theoretically and experimentally. Kinetic data also demonstrate the reaction might involve a concerted mechanism.

IV. EXPERIMENTAL

Melting points were uncorrected. IR spectra were recorded on a Nicolet (205) FT-IR spectrophotometer as neat films on KBr plates. ^1H NMR spectra were measured either on a JOEL PMX 60 SI (60 MHz), or a Brucker WM 250 (250 MHz) spectrometer. In all ^1H NMR measurements, chemical shifts were reference with tetramethylsilane $\delta = 0.00$ ppm. ^{13}C spectra were obtained on a Brucker WM 250 (62.9 MHz) spectrometer. Mass spectra were obtained on a VG 70-70 system at 20 eV unless otherwise noted. Elemental analyses were performed by the Medac Ltd, Department of Chemistry, Brunel University, U. K. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl immediately prior to use. The *N-tert*-butylhydroxylamine was dried under reduced pressure and stored under nitrogen in a freezer. All cycloadditions were run with the reaction mixture deoxygenated by the freeze-pump-thaw method (-195 to 25 °C, three cycles) in 8×10^{-2} M. Silica gel chromatographic purification were performed under air by flash chromatoraphy[42] with Merck 70-230 mesh silica packed in glass column.

UV-vis spectral and kinetic measurements were performed on a Hitachi U-3300 spectrophotometer equipped with a Neslab temperature controller RTE-210. The temperature was measured with a Fluke 2170A digital thermometer (± 0.1 °C) with type K thermal couple wire. The solvents used, hexane (CaH_2), THF (Na/benzophenone ketyl), acetone (K_2CO_3) and acetonitrile (CaH_2), were distilled prior to use. All the solvents and stock solutions were deoxygenated by the freeze-pump-thaw method (-195 to 25 °C, at least five cycles). Reactants were transferred inside a dry box to a Shlenk type UV-cuvette (Appendix III). The progress of reaction 13 was monitored spectrophotometrically at 486 nm for both **31b** and **31d**, and 502 nm for **31a**. Generally a tenfold excess of nitrone was used in order to establish pseduo-first-order conditions. Reactions were followed for at least 3 half-lives. The

corresponding rate constants were calculated using the Guggenheim method and the computer programme KaleidaGraph was employed to find out the slopes of linear straight lines.

Preparation of Alkynyl Carbene Complex: General procedure.[14] The preparation of the known (methoxy-2-phenylethynylmethylene)pentacarbonylchromium **(31a)**[14] was described as a typical example. A solution of n-butyllithium (1.6 M in hexane, 5.7 mL, 9.1 mmol) was added dropwise to phenylacetylene (1.0 mL, 9.1 mmol) in 10 mL of THF at 0 °C. After 45 min at 0 °C the solution was transferred dropwise (slowly) via cannula to a suspension of chromium hexacarbonyl (2.2 g 10.0 mmol) in THF (20 ml). After 1 h at room temperature, methyl triflate (1.3 mL, 11 mmol) was slowly added to the reaction mixture at 0 °C. When the addition was complete, the mixture was stirred for another 0.5 h at 0 °C. The reaction was quenched by adding 20 mL of $NaHCO_3$ (saturated solution) and stirred for 10 min. The organic layer was separated and the aqueous layer was extracted with ether (3 x 20 mL) times. The organic solution was combined, washed with water (30 mL) and brine (30 mL), and dried ($MgSO_4$). After removal of solvents, the crude product was flashed chromatographed on silica gel column using hexane as the eluent. Dark purple low melting solid (1.32 g, 3.9 mmol) was collected in 74 % yield. R_f (hexane) = 0.38; IR (KBr) 1950, 1995, 2070, 2160 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 4.43 (s, 3 H), 7.46-7.55 (m, 5 H).

Preparation of (Methoxy-2-phenylethynylmethylene)pentacarbonyltungsten (31b).[14] The black solid was collected in 41 % yield. R_f (hexane) = 0.35; IR (KBr) 1930, 1975, 2075, 2170 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 4.35 (s, 3 H), 7.50-7.57 (m, 5 H).

Preparation of (Methoxy-2-(4-methylphenyl)ethynylmethylene)-pentacarbonylchromium (31c). The dark purple solid was collected in 45 % yield. R_f (hexane) = 0.29; mp 107-108 °C (decomp); IR (thin film) 1933, 1979, 2058, 2149 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 2.40 (s, 3 H), 4.39 (s, 3 H), 7.24 (d, 2 H, J =

7.6 Hz), 7.47 (d, 2 H, J = 7.9 Hz); ^{13}C NMR (acetone-d_6, 62.9 MHz) 22.27, 67.73, 93.92, 118.88, 131.23, 134.28, 138.94, 144.85, 217.73, 226.71, 316.05; mass spectrum *m/z* (rel intensity) 350 (M^+, 7), 294 (M^+-2CO, 50), 266 (25), 238 (23), 210 (69); Anal. Calcd for $C_{16}H_{10}CrO_6$: C, 54.86; H, 2.86. Found: C, 54.91; H, 2.86.

Preparation of (Methoxy-2-(4-methylphenyl)ethynylmethylene)-pentacarbonyltungsten (31d). The dark solid was collected in 25 % yield. R_f (hexane) = 0.21; mp 107-108 °C (decomp); IR (thin film) 1882, 1914, 1940, 1983, 2146 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.40 (s, 3 H), 4.34 (s, 3 H), 7.26 (d, 2 H, J = 7.5 Hz), 7.53 (d, 2 H, J = 7.5 Hz); ^{13}C NMR (acetone-d_6, 62.9 MHz) 21.12, 66.69, 97.67, 117.71, 130.15, 133.29, 143,80, 197.57 ($J_{W,C}$ = 128.9 Hz), 205.09, 287.29; mass spectrum *m/z* (rel intensity) 482 (M^+, 47), 426 (M^+-2CO, 59), 396 (77), 370 (76), 342 (100); Anal. Calcd for $C_{16}H_{10}O_6W$: C, 39.86; H, 2.09. Found: C, 39.86; H, 2.07.

Preparation of (Methoxy-2-trimethylsilylethynylmethylene)penta-carbonylchromium (31e).[43] The black solid was collected in 62 % yield. ^{1}H NMR ($CDCl_3$, 60 MHz) δ 0.33 (s, 9 H), 4.36 (s, 3 H).

Preparation of (Methoxy-2-trimethylsilylethynylmethylene)penta-carbonyltungsten (31f).[43] The black solid was collected in 72 % yield. IR (KBr) 1996, 2072 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 0.35 (s, 9 H), 4.27 (s, 3 H).

Preparation of Methyl 2-phenylethynyl carboxylate (37). A solution of *n*-butyllithium (1.6 M in hexane, 18.8 mL, 30 mmol) was added to phenylacetylene (3.2 mL, 30 mmol) in 20 mL of THF at -78 °C. After 1 h at room temperature, methyl chloroformate (2.3 mL, 30 mmol) was slowly added to the solution at -78 °C. When the addition was complete, the mixture was stirred for another 1 h at room temperature. The resulting solution was then extracted with ether (30 mL), and the etheral extract was dried ($MgSO_4$). After removal of solvents, the crude mixture was chromatographed on silica gel column using hexane/dichloromethane (3:1) as the eluent to give a pale yellow liquid (3.1g, 65 %) upon removal of solvents. IR (thin film)

1435, 1445, 1495, 1715, 2240 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 3.78 (s, 3 H), 7.23-7.63 (m, 5 H).

Preparation of 2-Methyl-2-nitropropane (33).[20] To a well-stirred suspension of 220 g potassium permanganate in 1L of water, contained in a 2 L three-necked flask fitted with a reflux condenser, a mechanical stirrer, a thermometer, and a 250 mL dropping funnel, was added dropwise and with stirring over a 10 min period, 33.3 g (0.456 mol) of *tert*-butylamine. When the addition was complete, the reaction mixture was heated to 55 °C over a period of approx. 2 h., and then the reaction mixture was maintained at 55 °C with continuous stirring for 3 h. The dropping funnel and reflux condensers were replaced by a stopper and a still head fitted for steam distillation and the product was steam distilled from the reaction mixture. The liquid product was separated from the denser water layer and then diluted with 90 mL of ether and washed successively with two 50 mL portions of aqueous 2 M HCl acid and with 20 mL of water. After the ethereal solution has been dried over anhydrous magnesium sulfate, the ether was evaporated by rotatory evaporator. The crude product amounted to 23.3 g (50 %) and was sufficiently pure for use in the next step. It slowly solidified on standing to a waxy solid.

Preparation of *N-tert*-butylhydroxylamine (34).[20] Aluminum foil (17 g, thickness 0.005 cm) was cut into strips 5 cm by 25 cm, and each strip was rolled into a cylinder about 1 cm in diameter. Each of the aluminum foil cylinders was amalgamated by immersing it in a solution of 8.0 g (0.030 mol) of $HgCl_2$ in 400 mL of water for 15 seconds. Each amalgamated cylinder was then rinsed successively in ethanol and in ether and added to a mixture of 600 mL of ether and 6 mL of water contained in a 1 L three-necked flask fitted with a dropping funnel, a mechanical stirrer, and two efficient reflux condensers in series. The reaction mixture was stirred vigorously and 24.4 g (0.237 mol) of 2-methyl-2-nitropropane was added dropwise at such a rate that the ether refluxed briskly. The reaction usually exhibited a 5-7 minutes induction period after which a vigorous reaction occurs and cooling with an ice-bath was necessary. After addition of the nitro compound was complete, the reaction

mixture was stirred for an additional 30 min, and then the stirrer was stopped and the gelatinoius precipitate was allowed to settle. The colorless reaction solution was decanted through a glass wool plug into a 1 L separatory funnel and washed with two 100 mL portion of aqueous 2 M NaOH. The ppt in the reaction flask was washed with two 200 mL portion of ether and then washings are combined and washed with the aqueous NaOH solution. The combined etheral solution were dried over anhydrous sodium sulfate and concentrated under reduced pressure with a rotary evaporator. The residual crystalline solid was dried under reduced pressure at room temperature. The solid obtained was 5.1 g (24 %).

Preparation of *N-tert*-butyl nitrones. The nitrones were prepared by condensation of the appropriate aldehyde (10 mmol) with *N-tert*-butylhydroxylamine[20] (10 mmol) in 40 mL of solvent containing suspended anhydrous magnesium sulphate (2.0 g) under nitrogen, according to the procedure of Torssell and Zeuthen.[18] The reaction conditions are tabulated on Table III. After filtration and removal of solvents, the crude product was purified by flash chromatography on silica gel.

***N*-{(4-dimethylaminophenyl)methylene}-2-methyl-2-propanamine *N*-oxide (35a)** was obtained as yellow solid in 47 % yield; R_f (EtOAc) = 0.45; mp 134-136 °C; IR (KBr) 1104, 1126, 1188, 1357, 1520, 1602 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 1.56 (s, 9 H), 2.98 (s, 6 H), 6.66 (d, 2 H, J = 9.0 Hz), 7.35 (s, 1 H), 8.18 (d, 2 H, J = 9.0 Hz); mass spectrum (20 eV) *m/z* (rel intensity) 220 (M^+, 79), 204 (32), 189 (71), 164 (100), 148 (25); Anal. Calcd for $C_{13}H_{20}N_2O$: C, 70.87; H, 9.15; N, 12.72. Found: C, 70.91; H, 9.27; N, 12.73.

***N*-{(4-methoxyphenyl)methylene}-2-methyl-2-propanamine *N*-oxide (35b)** was obtained as yellow solid in 63 % yield; R_f (EtOAc) = 0.46; mp 94-96 °C (lit.[44] mp 94-96 °C); ^1H NMR ($CDCl_3$, 250 MHz) δ 1.54 (s, 9 H), 3.77 (s, 3 H), 6.86 (d, 2 H, J = 9.0 Hz), 7.41 (s, 1 H), 8.23 (d, 2 H, J = 8.9 Hz).

***N*-{(4-methylphenyl)methylene}-2-methyl-2-propanamine *N*-oxide (35c)** was obtained as yellow-brown solid in 90 % yield; R_f (hexane/EtOAc, 5:1) =

0.18; mp 70-73 °C (lit.[44] mp 70-73 °C); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.57 (s, 9 H), 2.34 (s, 3 H), 7.19 (d, 2 H, J = 8.0 Hz), 7.43 (s, 1 H), 8.15 (d, 2 H, J = 8.2 Hz).

***N*-{(4-methylphenyl)methylene}-2-methyl-2-propanamine *N*-oxide (35d)** can be purchased from Aldrich or prepared in excellent yield from oxidation of *N*-benzyl-*tert*-butylamine by hydrogen peroxide in the presence of sodium tungstate catalyst.[20]

***N*-{(4-bromophenyl)methylene}-2-methyl-2-propanamine *N*-oxide (35e)** was obtained as pale-yellow solid in 61 % yield; R_f (CH_2Cl_2) = 0.17; mp 60-62 °C (lit.[45] mp 61-62 °C); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.58 (s, 9 H), 7.49-7.53 (m, 3 H), 8.16 (d, 2 H, J = 9.1 Hz).

***N*-{(4-chlorophenyl)methylene}-2-methyl-2-propanamine *N*-oxide (35f)** was obtained as white solid in 75 % yield; R_f (hexane/EtOAc, 4:1) = 0.24; mp 72-73 °C (lit.[46] mp 112-115 °C); IR (KBr) 891, 1197, 1249, 1362, 1388, 1398, 1410, 1483, 1548 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.49 (s, 9 H), 7.26 (d, 2 H, J = 8.6 Hz), 7.43 (s, 1 H), 8.15 (d, 2 H, J = 8.6 Hz); mass spectrum *m/z* (rel intensity) 211 (M^+, 5), 155 (5), 57 (100); Anal. Calcd for $C_{11}H_{14}ClNO$: C, 62.24; H, 6.61; N, 6.62. Found: C, 62.20; H, 6.62; N, 6.49.

Preparation of *N*-Methyl nitrones. The nitrones were prepared by condensation of the appropriate aldehyde (10 mmol) with *N*-methylhydroxylamine hydrochloride (10 mmol) in 40 mL of dichloromethane containing suspended anhydrous magmesium sulphate (2.0 g) and sodium bicarbonate (1.1 g) in refluxing CH_2Cl_2 for 24 h. The workup procedure was same as that of preparation of *N-tert*-butyl nitrone **32a-f.**

***N*-{(4-dimethylaminophenyl)methylene}-Methanamine *N*-oxide (32a)** was obtained as pale orange solid in 87 % yield; R_f (EtOAc/MeOH, 10:1) = 0.25; mp 114-116 °C (lit.[47] mp 131.5-134 °C); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.00 (s, 6 H), 3.77 (s, 3 H), 6.66 (d, 2 H, J = 9.0 Hz), 7.17 (s, 1 H), 8.10 (d, 2 H, J = 9.1 Hz).

***N*-{(4-methoxyphenyl)methylene}-Methanamine *N*-oxide (32b)** was obtained as pale yellow hydroscopic solid in 80 % yield; R_f (EtOAc) = 0.10; mp 57-59 °C (lit.[48] mp 69-70 °C); ^{1}H NMR ($CDCl_3$, 250 MHz) 3.82 (s, 6 H), 6.91 (d, 2 H, J = 9.0 Hz), 7.27 (s, 1 H), 8.19 (d, 2 H, J = 9.0 Hz).

***N*-{(4-methylphenyl)methylene}-Mehtanamine *N*-oxide (32c)** was obtained as pale yellow solid in 87 % yield; R_f (EtOAc) = 0.15; mp 114-115 °C (lit.[47] mp 116.5-118.5 °C); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 2.35 (s, 3 H), 3.83 (s, 3 H), 7.20 (d, 2 H, J = 8.1 Hz), 7.30 (s, 1 H), 8.09 (d, 2 H, J = 8.2 Hz).

***N*-phenyl methylene-Methanamine *N*-oxide (32d)** was obtained as yellow solid in 85 % yield; R_f (EtOAc) = 0.14; mp 72-75 °C (lit.[49] mp 82.5-83 °C); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.84 (s, 3 H), 7.34-7.39 (m, 4 H), 8.16-8.20 (m, 2 H).

***N*-{(4-bromophenyl)methylene}-Methanamine *N*-oxide (32e)** was obtained as white solids: yield 70 %; R_f (EtOAc) = 0.10; mp 129-130 °C (lit.[49] mp 129.5-130 °C); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.85 (s, 3 H), 7.32 (s, 1 H), 7.52 (d, 2 H, J = 8.7 Hz), 8.08 (d, 2 H, J = 8.7 Hz).

***N*-{(4-chlorophenyl)methylene}-Methanamine *N*-oxide (32f)** was obtained as pale yellow solid in 73 % yield; R_f (EtOAc) = 0.10; mp (CH_2Cl_2/hexane) 125-127 °C (lit.[49] mp 130-131 °C); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.86 (s, 3 H), 7.37 (d, 2 H, J = 8.8 Hz), 7.34 (s, 1 H), 8.16 (d, 2 H, J = 8.7 Hz).

***N*-{(4-cyanophenyl)methylene}-Methanamine *N*-oxide (32g)** was obtained as white solid in 90 % yield; R_f (acetone) = 0.58; mp (CH_2Cl_2/hexane) 186-187 °C (lit.[49] mp 187 °C); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.91 (s, 3 H), 7.43 (s, 1 H), 7.67 (d, 2H, J = 8.6 Hz), 8.26 (d, 2 H, J = 8.6 Hz).

***N*-{(4-nitrophenyl)methylene}-Methanamine *N*-oxide (32h)** was obtained as white solid in 90 % yield; mp (CH_2Cl_2) 207-209 °C (lit.[49] mp 206-207 °C); ^{1}H NMR ($CDCl_3$, 250 MHz) δ 3.93 (s, 3 H), 7.50 (s, 1 H), 8.24 (d, 2 H, J = 9.0 Hz), 8.36 (d, 2 H, J = 9.1 Hz).

Reaction of Alkynyl Carbene Complex with Nitrone. General procedure. A solution of the chromium complex **31a** (54 mg, 161 μmol) and the nitrone, H-PBN **35d** (29 mg, 164 μmol) in THF (2 mL) was stirred at room temperature under nitrogen. The reaction was closely monitored by TLC. The red solution changed to orange after 3 h. The solvent was then evaporated and the residue was flashed chromatographed on silica gel with dichloromethane/hexane (1:1) to give the red viscous oil **40d** (79 mg, 95 %). R_f (hexane/CH_2Cl_2, 1:1) = 0.77; IR (KBr) 1935, 1959, 1996, 2061 cm^{-1}; ^1H NMR (acetone-d_6, 250 MHz) δ 1.27 (s, 9 H), 4.34 (s, 3 H), 6.08 (s, 1 H) and 7.26-7.70 (m, 10 H); ^{13}C NMR (acetone-d_6, 50 MHz) δ 26.57, 63.20, 66.04, 73.91, 129.52, 129.80, 130.32, 130.64, 130.92, 132.89, 218.53, 215.43, 339.28; mass spectrum *m/z* (rel intensity) 429 ([M-3CO]$^+$, 1), 373 (2), 279 (18), 261 (21), 204 (64), 146 (54), 105 (100); Anal. Calcd for $C_{26}H_{23}CrNO_7$: C, 60.82; H, 4.52; N, 2.73. Found: C, 60.40; H, 4.17; N, 2.90.

Reaction of Complex 31a with NMe_2-PBN 35a. The reaction mixture was stirred for 15 min. The red viscous oil **40a** was collected in 94 % yield. R_f (hexane/CH_2Cl_2, 2:1) = 0.42; IR (thin film) 1933, 2059 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 1.27 (br s, 9 H), 2.91 (br s, 3 H), 3.97 (br s, 1 H), 6.11 (br s, 1 H), 6.68-7.40 (br m, 9 H); mass spectrum *m/z* (rel intensity) 500 ([M-2CO]$^+$, 1), 472 (4), 444 (1), 416 (5), 380 (9).

Reaction of Complex 31a with MeO-PBN 35b. The reaction mixture was stirred for 30 min. The red viscous oil **40b** was collected in 90 % yield. R_f (hexane/CH_2Cl_2, 1:1) = 0.44; IR (thin film) 1936, 2059 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 1.27 (s, 9 H), 3.78 (s, 3 H), 4.02 (s, 1 H), 6.12 (s, 1 H), 6.81-7.41 (m, 9 H); Anal. Calcd for $C_{27}H_{25}CrNO_8$: C, 59.67; H, 4.64; N, 2.58. Found: C, 59.36; H, 4.73; N, 2.58.

Reaction of Complex 31a with Me-PBN 35c. The reaction mixture was stirred for 40 min. The red viscous oil **40c** was collected in 98 % yield. R_f (hexane/CH_2Cl_2, 1:1) = 0.53; IR (thin film) 1939, 1984, 2059 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 1.26 (s, 9 H), 2.30 (s, 3 H), 3.97 (s, 3 H), 6.12 (s, 1 H), 7.14-

7.40 (m, 9 H); mass spectrum *m/z* (rel intensity) 471 ([M-2CO]$^+$, 0.3), 443 (4.0), 415 (0.8), 387 (9.6) 372 (12.5); Anal. Calcd for $C_{27}H_{25}CrNO_7$: C, 61.48; H, 4.78; N, 2.66. Found: C, 61.32; H, 4.92; N, 2.59.

Reaction of Complex 31a with Br-PBN 35e. The reaction mixture was stirred for 5 h. The red viscous oil **40e** was collected in 94 % yield. R_f (hexane/CH_2Cl_2, 2:1) = 0.85; IR (thin film) 1937, 2066 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.24 (s, 9 H), 4.07 (s, 3 H), 6.07 (s, 1 H), 7.29-7.48 (m, 9 H); mass spectrum *m/z* (rel intensity) 509 ([M-3CO]$^+$, 1.8), 507 (1.5), 451 (3.4), 417 (6.0), 415 (6.4); Anal. Calcd for $C_{26}H_{22}BrCrNO_7$: C, 52.72; H, 3.74; N, 2.36. Found: C, 52.72; H, 3.93; N, 2.12.

Reaction of Complex 31a with Cl-PBN 35f. The reaction mixture was stirred for 5 h. The red viscous oil **40f** was collected in 99 % yield. R_f (hexane/CH_2Cl_2, 4:1) = 0.33; IR (thin film) 1940, 2059 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.24 (br s, 9 H), 4.07 (br s, 3 H), 6.08 (br s, 1 H), 7.34-7.41 (br m, 9 H); mass spectrum *m/z* (rel intensity) 407 ([M-5CO]$^+$, 0.2), 371 (1.5), 207 (12.2), 204 (10.8), 182 (22.8), 180 (67.7); Anal. Calcd for $C_{26}H_{22}ClCrNO_7$: C, 57.00; H, 4.05; N, 2.57. Found: C, 57.30; H, 4.22; N, 2.49.

Reaction of Complex 31b with NMe_2-PBN 35a. The reaction mixture was stirred for 5 min. The red viscous oil **41a** was collected in 99 % yield. R_f (hexane/CH_2Cl_2, 1:1) = 0.25; IR (thin film) 1925, 1977, 2063 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.25 (s, 9 H), 2.91 (s, 6 H), 4.15 (s, 3 H), 5.92 (s, 1 H), 6.69-6.72 (m, 2 H), 7.22-7.25 (m, 2 H), 7.43-7.55 (m, 5 H); mass spectrum *m/z* (rel intensity) 662 ([M-CO]$^+$, 0.3), 602 (2.2), 322 (1.9), 279 (0.6); Anal. Calcd for $C_{28}H_{28}N_2O_7W$: C, 48.85; H, 4.10; N, 4.07. Found: C, 48.55; H, 4.10; N, 3.99.

Reaction of Complex 31b with MeO-PBN 35b. The reaction mixture was stirred for 15 min. The red viscous oil **41b** was collected in 95 % yield. R_f (hexane/CH_2Cl_2, 1:1) = 0.46; IR (thin film) 1920, 1977, 2063 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.22 (s, 9 H), 3.76 (s, 3 H), 4.16 (s, 3 H), 5.91 (s, 1 H), 6.85-6.89 (d, 2 H), 7.41-7.54 (m, 5 H), 7.26-7.31 (d, 2 H); mass spectrum *m/z* (rel

intensity) 590 ([M-3CO]$^+$, 9.0), 535 (4.1), 477 (8.9), 464 (8.3) 434 (6.6); Anal. Calcd for $C_{27}H_{25}NO_8W$: C, 48.02; H, 3.73; N, 2.07. Found: C, 48.42; H, 3.82; N, 2.05.

Reaction of Complex 31b with Me-PBN 35c. The reaction mixture was stirred for 40 min. The red viscous oil **41c** was collected in 95 % yield. R_f (hexane/EtOAc, 10:1) = 0.43; IR (thin film) 1916, 2063 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.25 (s, 9 H), 2.32 (s, 3 H), 4.18 (s, 3 H), 5.94 (s, 1 H), 7.41-7.54 (m, 5 H), 7.26-7.31 (d, 2 H); mass spectrum *m/z* (rel intensity) 631 ([M-CO]$^+$, 14.5), 603 (1.8), 575 (65.6), 547 (2.6), 519 (39.3); Anal. Calcd for $C_{27}H_{25}NO_7W$: C, 49.18; H, 3.82; N, 2.12. Found: C, 48.83; H, 3.88; N, 2.12.

Reaction of Complex 31b with H-PBN 35d. The reaction mixture was stirred for 3 h. The red viscous oil **41d** was collected in 92 % yield. R_f (hexane/CH_2Cl_2, 4:1) = 0.18; IR (thin film) 1919, 2063 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.20 (s, 9 H), 4.13 (s, 3 H), 5.91 (s, 1 H), 7.21-7.53 (m, 10 H); ^{13}C NMR ($CDCl_3$, 62.5 MHz) δ 25.16, 61.68, 67.45, 71.70, 127.79, 128.55, 128.65, 128.90, 129.60, 132.95, 142.85, 160.29, 197.38 ($J_{W,C}$ = 63.9 Hz), 202.12, 303.04; mass spectrum *m/z* (rel intensity) 645 (M$^+$, 0.45), 617 (4.8), 563 (15.2), 561 (18.0), 505 (14.9); HRMS Calcd for $C_{26}H_{23}NO_7W$ 645.0978, found 645.0931.

Reaction of Complex 31b with Br-PBN 35e. The reaction mixture was stirred for 5 h. The red viscous oil **41e** was collected in 99 % yield. R_f (hexane/CH_2Cl_2, 1:1) = 0.56; IR (thin film) 1918, 2064 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.20 (s, 9 H), 4.20 (s, 3 H), 5.88 (s, 1 H), 7.26-7.55 (m, 9 H); mass spectrum *m/z* (rel intensity) 637 ([M-2CO]$^+$,2.6), 585 (1.7), 344 (0.7), 224 (17.2), 184 (8.2); Anal. Calcd for $C_{26}H_{22}BrNO_7W$: C, 43.12; H, 3.06; N, 1.93. Found: C, 43.11; H, 3.19; N, 1.91.

Reaction of Complex 31b with Cl-PBN 35f. The reaction mixture was stirred for 5 h. The red viscous oil **41f** was collected in 96 % yield. R_f (hexane/CH_2Cl_2, 1:1) = 0.63; IR (thin film) 1924, 1978, 2064 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 1.20 (s, 9 H), 4.19 (s, 3 H), 5.89 (s, 1 H), 7.24-7.54 (m, 9 H);

mass spectrum *m/z* (rel intensity) 623 ([M-CO]$^+$, 0.3), 595 (4.0), 594 (11.6), 567 (0.4), 539 (7.2), 483 (13.8); Anal. Calcd for $C_{26}H_{22}ClNO_7W$: C, 45.94; H, 3.26; N, 2.06. Found: C, 46.23; H, 3.35; N, 2.03.

Reaction of Complex 31a with PBnN 36. The reaction was stirred for 10 min. The product was very unstable when the solvent was removed at room temperature. The hexane/EtOAc eluate was removed over vacuum at 0 °C. The red liquid **42a** was collected in 73 % yield. ^{1}H NMR (acetone-d_6, 250 MHz) δ 4.34 (s, 3 H), 4.56 (dd, 2 H, J = 13, 33 Hz), 6.08 (s, 1 H), 7.28-7.52 (m, 15 H)

Reaction of Complex 31b with PBnN 36. The reaction was stirred for 10 min and red viscous oil **42b** was obtained in 92 % yield. R_f (hexane/CH_2Cl_2, 2:1) = 0.45; IR (thin film) 1939, 2064 cm^{-1}; ^{1}H NMR ($CDCl_3$, 250 MHz) δ 4.24 (s, 3 H), 4.42 (dd, 2 H, J = 13, 53 Hz), 5.84 (s, 1 H), 7.20-7.53 (m, 15 H).

Reaction of Complex 31b with NMe_2-PMN 32a. The reaction mixture was stirred for 5 min for the titled reaction and other PMNs unless otherwise noted. The red viscous oil **39a** was collected in 50 % yield. R_f (hexane/EtOAc, 5:2) = 0.33; IR (thin film) 1908, 2067 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 2.92 (s, 6 H), 3.00 (s, 3 H), 4.18 (s, 3 H), 5.53 (s, 1 H), 6.73-7.43 (m, 9 H).

Reaction of Complex 31b with MeO-PMN 32b. The red viscous oil **39b** was collected in 65 % yield. R_f (hexane/EtOAc, 10:1) = 0.10; IR (thin film) 1920, 1977, 2063 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 3.03 (s, 3 H), 3.78 (s, 3 H), 4.22 (s, 3 H), 5.58 (s, 1 H), 6.82-7.48 (m, 9 H).

Reaction of Complex 31b with Me-PMN 32c. The red viscous oil **39c** was collected in 85 % yield. R_f (hexane/CH_2Cl_2, 3:1) = 0.25; IR (thin film) 1921, 1978, 2064 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 2.31 (s, 3 H), 3.03 (s, 3 H), 4.20 (s, 3 H), 5.57 (s, 1 H), 7.13-7.51 (m, 9 H).

Reaction of Complex 31b with H-PMN 32d. The red viscous oil **39d** was collected in 86 % yield. R_f (hexane/EtOAc, 10:1) = 0.21; mp (ethanol) 94.5 °C; IR (thin film) 1919, 2065 cm^{-1}; ^{1}H NMR (benzene-d_6, 250 MHz) δ 2.71 (s, 3 H),

3.64 (s, 3 H), 5.49 (s, 1 H), 7.00-7.41 (m, 10 H); Anal. Calcd for $C_{23}H_{17}NO_7W$: C, 45.80; H, 2.84; N, 2.32. Found: C, 45.62; H, 2.84; N, 2.27.

Reaction of Complex 31b with Br-PMN 32e. The red viscous oil **39e** was collected in 97 % yield. R_f (hexane/CH_2Cl_2, 2:1) = 0.44; IR (thin film) 1925, 2064 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 2.98 (s, 3 H), 4.17 (s, 3 H), 5.48 (s, 1 H), 7.15-7.44 (m, 9 H).

Reaction of Complex 31b with Cl-PMN 32f. The red viscous oil **39f** was collected in 75 % yield. R_f (hexane/EtOAc, 10:1) = 0.40; IR (thin film) 1922, 2064 cm^{-1}; ^1H NMR ($CDCl_3$, 60 MHz) δ 3.05 (s, 3 H), 4.24 (s, 3 H), 5.57 (s, 1 H), 7.21-7.52 (m, 9 H); Anal. Calcd for $C_{23}H_{16}ClNO_7W$: C, 43.32; H, 2.53; N, 2.20. Found: C, 43.60; H, 2.76; N, 2.10.

Reaction of Complex 31b with CN-PMN 32g. The reaction mixture was stirred for 1 h. The red viscous oil **39g** was collected in 91 % yield. R_f (hexane/EtOAc, 10:1) = 0.12; IR (thin film) 1940, 1980, 2075 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 2.98 (s, 3 H), 4.17 (s, 3 H), 5.50 (s, 1 H), 7.18-7.45 (m, 9 H); Anal. Calcd for $C_{24}H_{16}N_2O_7W$: C, 45.88; H, 2.57; N, 4.46. Found: C, 45.46; H, 2.57; N, 4.37.

Reaction of Complex 31b with NO_2-PMN 32f. 15 mL solvent used instead of 2 mL as **32f** was less soluble in THF and the reaction mixture was stirred for 5 h. The red viscous oil **39h** was collected in 90 % yield. R_f (hexane/EtOAc, 10:1) = 0.29; IR (thin film) 1921, 2065 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 3.08 (s, 3 H), 4.26 (s, 3 H), 5.65 (s, 1 H), 7.41-7.56 (m, 2 H), 8.20-8.23 (m, 7 H); Anal. Calcd for $C_{23}H_{16}N_2O_9W$: C, 42.59; H, 2.47; N, 4.32. Found: C, 42.69; H, 2.64; N, 4.40.

Reaction of Complex 31c with H-PBN 35d. The reaction mixture was stirred for 3.5 h. The red viscous oil **43a** was collected in 88 % yield. R_f (hexane) = 0.15; IR (thin film) 1939, 1984, 2059 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 1.27 (s, 9 H), 2.38 (s, 3 H), 3.97 (s, 3 H), 6.13 (s, 1 H), 7.20-7.43 (m, 9 H); mass spectrum (70 eV) *m/z* (rel intensity) 443 ([M-3CO]$^+$, 2), 387 (2) 351 (9), 274 (27), 218 (100);

Anal. Calcd for $C_{27}H_{25}CrNO_7$: C, 61.48; H, 4.78; N, 2.66. Found: C, 61.76; H, 4.90; N, 2.61.

Reaction of Complex 31d with H-PBN 35d. The reaction mixture was stirred for 1 h. The red viscous oil **43b** was collected in 95 % yield. R_f (hexane/CH_2Cl_2, 4:1) = 0.2; IR (thin film) 1939, 1984, 2059 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz) δ 1.25 (s, 9 H), 2.43 (s, 3 H), 4.27 (s, 3 H), 5.91 (s, 1 H), 7.51-7.63 (m, 9 H).

Reaction of Complex 31e with H-PBN 35d. The reaction mixture was heated to 50 °C in a Schlenck tube for 18 h. After removal of solvent, the crude prodcut was chromatographed in silica gel column using hexane/ethyl acetate (10:1) as eluent. The red solids **44a** was collected in 26 % yield. mp 95-99 °C; IR (KBr) 1910, 1952, 1978, 2054 cm^{-1}; ^1H NMR (acetone-d_6, 250 MHz) δ 0.38 (s, 9 H), 1.26 (s, 9 H), 4.73 (s, 3 H), 6.14 (s, 1 H), 7.23-7.45 (m, 5 H); mass spectrum, *m/z* (rel intensity) 425 ([M-3CO]$^+$, 6), 369 (4), 354 (14), 207 (16), 146 (96), 75 (100).

Reaction of Complex 31f with H-PBN 35d. The red solids **44b** was collected in 35 % yield. mp 99-101 °C; IR (KBr) 1899, 1934, 1982, 2061 cm^{-1}; ^1H NMR (benzene-d_6, 250 MHz) δ 0.08 (s, 9 H), 1.11 (s, 9 H), 3.83 (s, 3 H), 6.14 (s, 1 H), 6.97-7.32 (m, 5 H); ^{13}C NMR (benzene-d_6, 62.9 MHz) δ -1.68, 25.36, 61.84,66.92, 69.46, 128.54, 129.15, 144.01, 146.94, 171.00, 191.15, 198.29, 201.60, 295.28; mass spectrum, *m/z* (rel intensity) 644 (0.5), 641 (0.6), 640 (M$^+$, 2), 559 (20), 557 (25), 555 (16), 556 (10), 500 (2), 444 (26), 400 (21), 340 (23), 146 (100).

APPENDIX I

Guggenheim's Method:[29]

The method is applicable to a first-order reaction followed by a physical measurement where the equilibrium or final reading cannot be made. If times t_1, t_2, t_3, etc., and $t_1 + \Delta$, $t_2 + \Delta$, $t_3 + \Delta$, etc., are selected where Δ is a constant increament, then the following equations are true:

$$(\lambda_1 - \lambda_\infty) = (\lambda_0 - \lambda_\infty)\, e^{-kt_1} \qquad (1)$$

$$(\lambda'_1 - \lambda_\infty) = (\lambda_0 - \lambda_\infty)\, e^{-k(t_1+\Delta)} \qquad (2)$$

where λ_1 and λ'_1 are readings of a suitable physical property at t_1 and $t_1 + \Delta$, respectively, and the usual first order equation is written in exponential form. Similar equations would be true for t_2 and $t_2 + \Delta$. Subtracting (2) from (1) gives

$$(\lambda_1 - \lambda'_1) = (\lambda_0 - \lambda_\infty)\, e^{-kt_1}\,(1-e^{-k\Delta}) \qquad (3)$$

or

$$kt_1 + \ln (\lambda_1 - \lambda'_1) = \ln [(\lambda_0 - \lambda_\infty)(1-e^{-k\Delta})] \qquad (4)$$

$$= \text{a constant}$$

which can be generalized by dropping the subscript 1. Before this method can be used it must be certain that the reaction is simple first-order, since certain other more complex reactions (reversible and concurrent first-order reactions) will give apparent rate constants by this method. The interval Δ should be two or three times as great as the half-period of the reaction for accuracy.

APPENDIX II

A Demonstration of Determination of Rate Constants k_{obs} or k:

After obtaining the data from Time Scan (Figure 3, reaction 13 of carbene complex **31b** (6.0×10^{-5} M) and PBN **35d** (12.03×10^{-3} M) in hexane at 15.2 °C), a range of selected intervals of absorbance was picked up as List I. Generally, the half-life of the reaction was first estimated. For example, the half-life of reaction represented by Figure 3 was about 550 s. So, we chose Δ as 1200 s (Δ is equal to 2-3 half-lives for accuracy, see Appendix I and the corresponding reference) and a plot of ln (A-A'), where $A'=A_{t+\Delta}$, *vs* time over 2 half-lives (time range: 20-1140 s) was produced by KaleidaGraph (version 2.1). The data and the graph are shown in Table A and Figure A respectively.

Date :03/17/94 11:09 PM
Sample :MLY 341
Comment :W + PBN at 15 oC (Hexane)

Wavelength :486.00 nm

No.	Time (sec)	Data (Abs)
1	0.0	0.8737
2	40.0	0.8461
3	80.0	0.8203
4	120.0	0.7958
5	160.0	0.7726
6	200.0	0.7508
7	240.0	0.7303
8	280.0	0.7111
9	320.0	0.6927
10	360.0	0.6755
11	400.0	0.6593
12	440.0	0.6440
13	480.0	0.6295
14	520.0	0.6157
15	560.0	0.6030
16	600.0	0.5907
17	640.0	0.5792
18	680.0	0.5683
19	720.0	0.5580
20	760.0	0.5483
21	800.0	0.5391
22	840.0	0.5304
23	880.0	0.5223
24	920.0	0.5145
25	960.0	0.5073
26	1000.0	0.5004
27	1040.0	0.4938
28	1080.0	0.4877
29	1120.0	0.4818
30	1160.0	0.4764
31	1200.0	0.4711
32	1240.0	0.4662
33	1280.0	0.4616
34	1320.0	0.4572
35	1360.0	0.4531
36	1400.0	0.4491
37	1440.0	0.4455
38	1480.0	0.4420
39	1520.0	0.4386
40	1560.0	0.4355
41	1600.0	0.4326
42	1640.0	0.4298
43	1680.0	0.4271
44	1720.0	0.4246
45	1760.0	0.4222
46	1800.0	0.4200
47	1840.0	0.4179
48	1880.0	0.4159
49	1920.0	0.4140
50	1960.0	0.4122
51	2000.0	0.4105
52	2040.0	0.4089
53	2080.0	0.4074
54	2120.0	0.4060
55	2160.0	0.4046
56	2200.0	0.4034
57	2240.0	0.4021
58	2280.0	0.4010
59	2320.0	0.3999
60	2360.0	0.3989
61	2400.0	0.3979
62	2440.0	0.3970
63	2480.0	0.3961
64	2520.0	0.3953
65	2560.0	0.3945
66	2600.0	0.3938
67	2640.0	0.3931
68	2680.0	0.3924
69	2720.0	0.3918
70	2760.0	0.3912
71	2800.0	0.3907
72	2840.0	0.3901
73	2880.0	0.3896
74	2920.0	0.3891
75	2960.0	0.3887
76	3000.0	0.3883
77	3040.0	0.3878
78	3080.0	0.3875
79	3120.0	0.3871
80	3160.0	0.3867
81	3200.0	0.3864
82	3240.0	0.3860
83	3280.0	0.3857
84	3320.0	0.3855
85	3360.0	0.3852
86	3400.0	0.3850
87	3440.0	0.3847
88	3480.0	0.3845
89	3520.0	0.3843
90	3560.0	0.3840
91	3600.0	0.3838

List I

	t (s)	A	A'	A-A'	ln(A-A')
1	20	0.8737	0.4711	0.4026	-0.9098
2	100	0.8203	0.4616	0.3587	-1.0253
3	180	0.7726	0.4531	0.3195	-1.1410
4	260	0.7303	0.4455	0.2848	-1.2560
5	340	0.6927	0.4386	0.2541	-1.3700
6	420	0.6593	0.4326	0.2267	-1.4841
7	500	0.6295	0.4271	0.2024	-1.5975
8	580	0.6030	0.4222	0.1808	-1.7104
9	660	0.5792	0.4179	0.1613	-1.8245
10	740	0.5580	0.4140	0.1440	-1.9379
11	820	0.5391	0.4105	0.1286	-2.0510
12	900	0.5223	0.4074	0.1149	-2.1637
13	980	0.5073	0.4046	0.1027	-2.2759
14	1060	0.4938	0.4021	0.0917	-2.3892
15	1140	0.4818	0.3999	0.0819	-2.5023

Table A

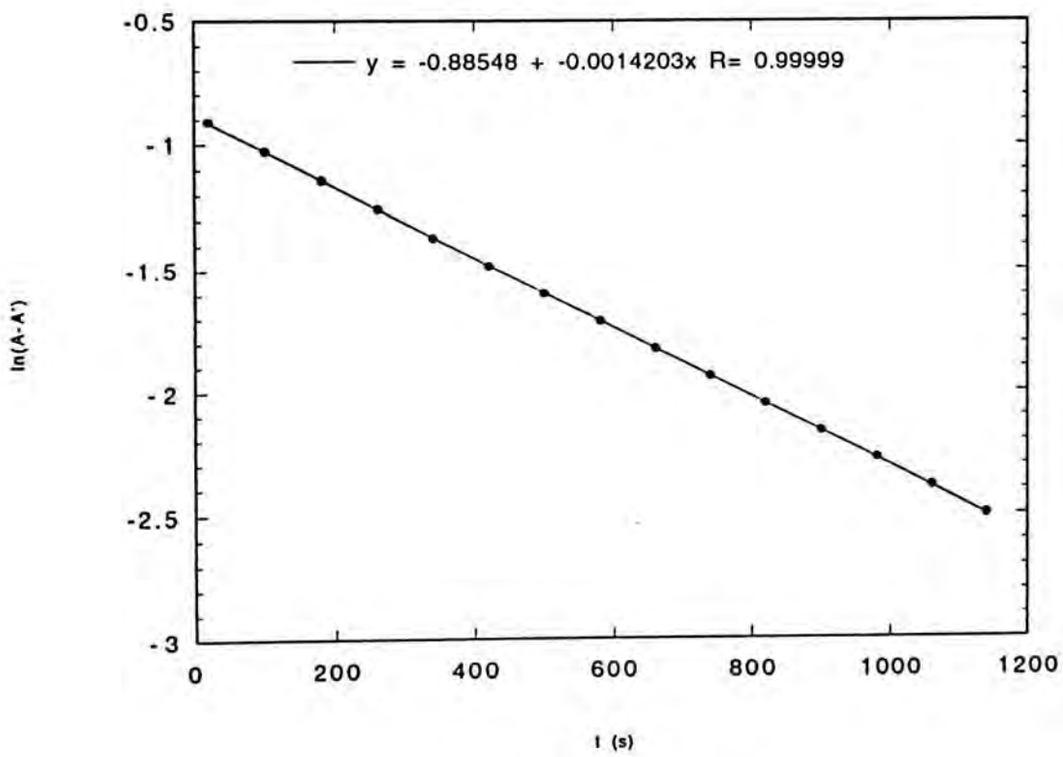
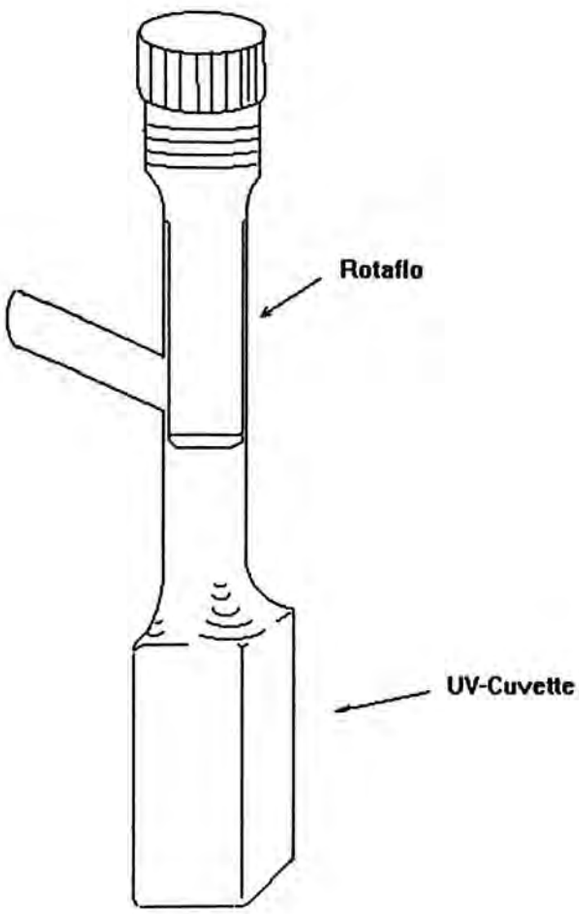


Figure A

The slope of the linear pseudo-first-order plot (r = 0.9999) is equal to k_{obs}, which when divided by [nitrone]$_{initial}$, will yield the rate constant k. In this example, k_{obs} = 1.420 x 10^{-3} s^{-1} and $k = k_{obs}$ / [nitrone]$_{initial}$ (or 1.420 x 10^{-3} s^{-1}/ 12.03 x 10^{-3} M), hence the rate constant k is found to be 0.1181 M^{-1} s^{-1}.

APPENDIX III



Schlenk Type Cuvette

APPENDIX IV

Data Collection and Processing Parameters:

Molecular formula	$C_{23}H_{17}NO_7W$
Molecular weight	603.23
Color and habit	red plate
Crystal size	0.05 x 0.30 x 0.40 mm^3
Crystal system	triclinic
Space group	$P\bar{1}$ (No. 2)
Unit cell parameters	a = 7.476(1) Å α = 97.26(3) °
	b = 12.364(2) β = 98.95(3)
	c = 13.354(2) γ = 105.77(3)
	V = 1154.8(4) $Å^3$ Z = 2 $F(000)$ = 584
Density (calcd)	1.735 g cm^{-3}
Radiation	graphite-monochromatized Mo$K\alpha$, λ = 0.71073 Å
Standard reflections	(1,0,4);(1,0,$\bar{4}$);(1,0,3)
Intensity variation	±1.3%
R_{int} (from merging of eqiv. reflections)	0.030
Absorption coefficient	5.04 mm^{-1}
Mean μr	0.63
Transmission factors	0.237 to 0.385
Scan type and rate	ω-scan; 5.0-60.0 deg min^{-1}
Scan range	0.60° below $K\alpha_1$ to 0.70° above $K\alpha_2$
Background counting	stationary counts for one-fourth of scan time at each end of scan range
Collection range	$0 \le h \le 8$, $-14 \le k \le 13$, $-15 \le \ell \le 14$; $2\theta_{max}$ = 50°
Unique data measured	3582
Obs. data with $\|F_o\| \ge 3\sigma(\|F_o\|)$, n	2964
No. of variables, p	302
Weighting scheme	$w = [\sigma^2\|F_o\| + 0.0012\|F_o\|^2]^{-1}(1-\exp[-8(\sin\theta/\lambda)^2])$
$R_F = \sum\|\|F_o\| - \|F_o\|\| / \sum\|F_o\|$	0.044
$wR = [\sum w(\|F_o\| - \|F_c\|)^2 / \sum w\|F_o\|^2]^{1/2}$	0.053
$S = [\sum w(\|F_o\| - \|F_c\|)^2/(n-p)]^{1/2}$	0.82
Largest and mean Δ/σ	.126, .004
Residual extrema in final difference map	+1.34 to -1.01 $eÅ^{-3}$

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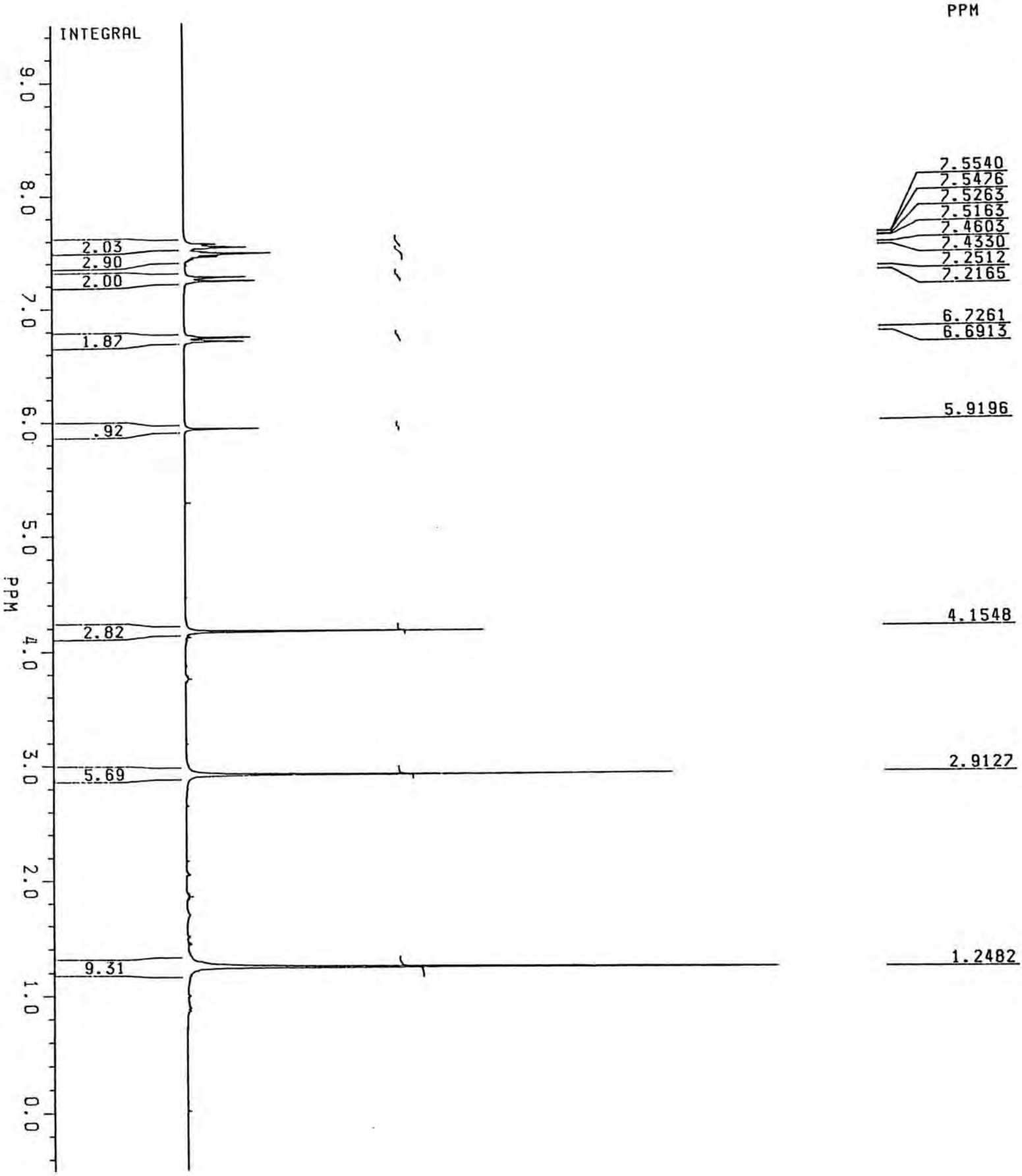
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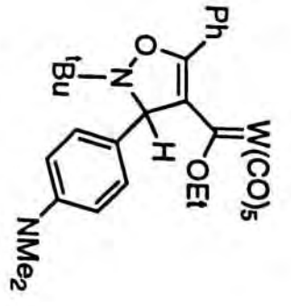
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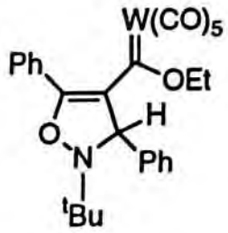

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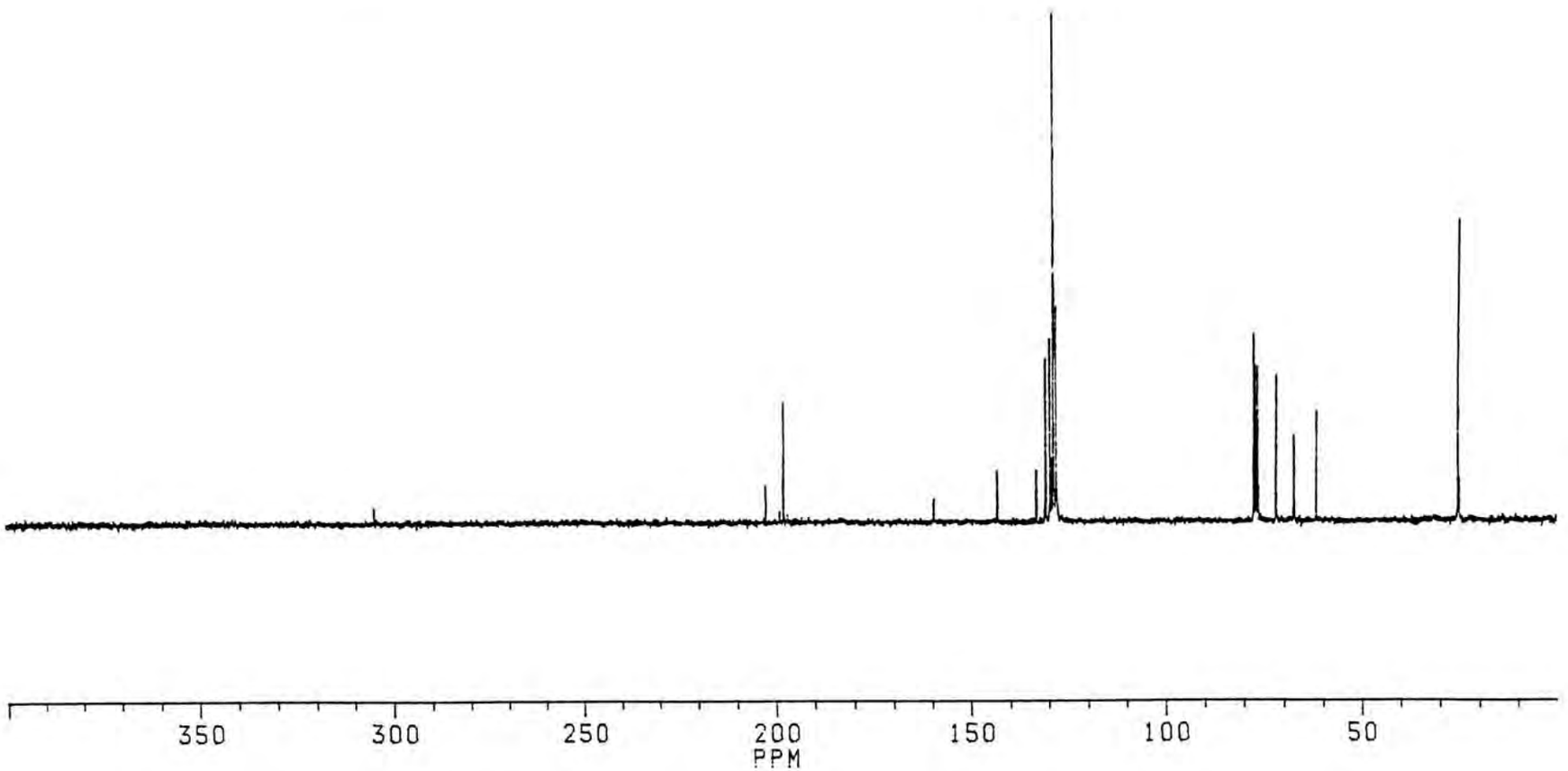

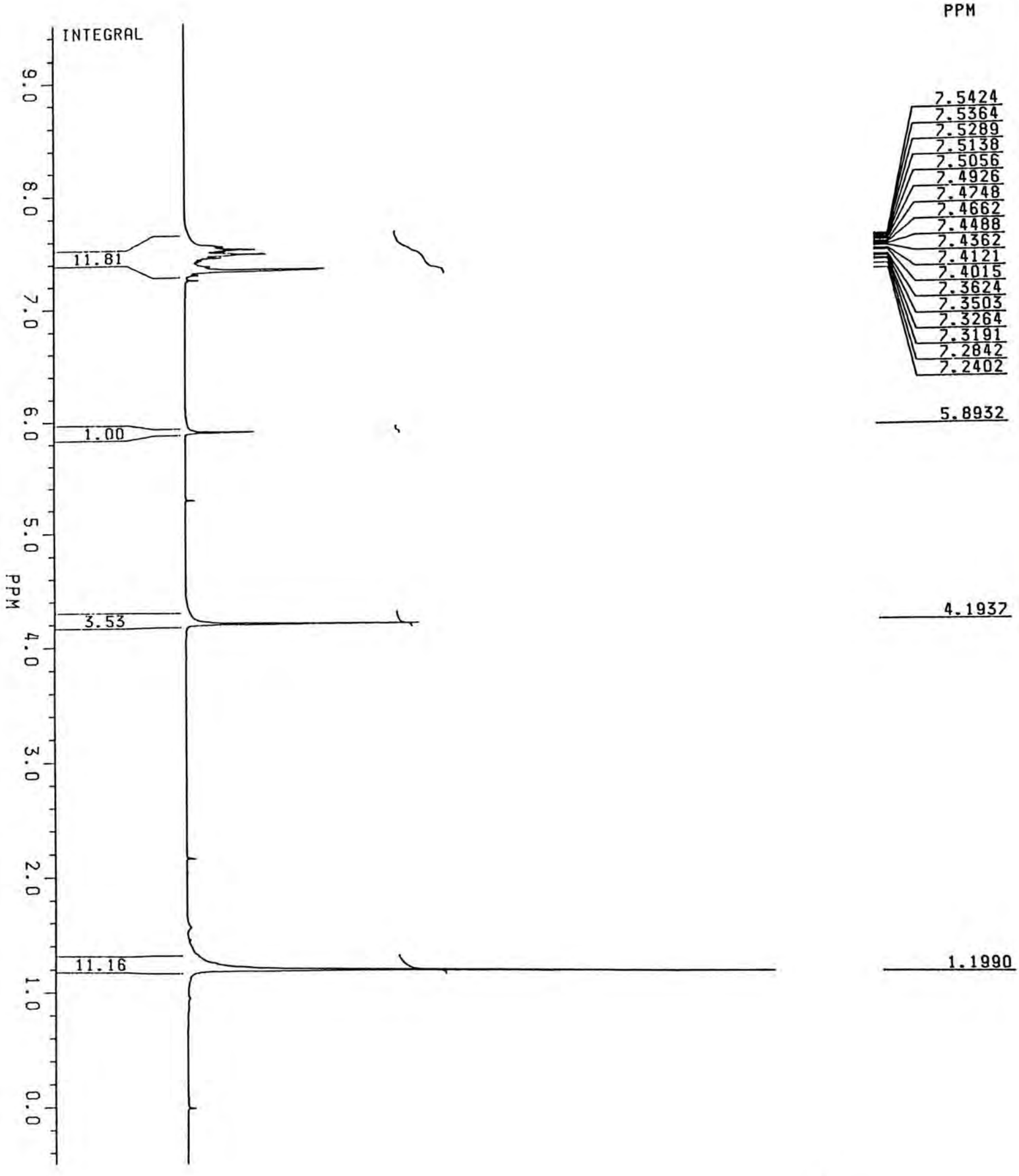
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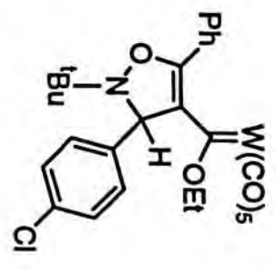
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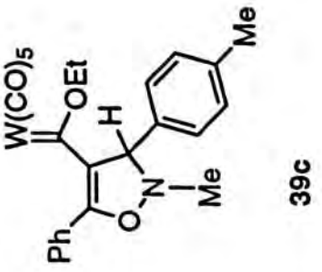
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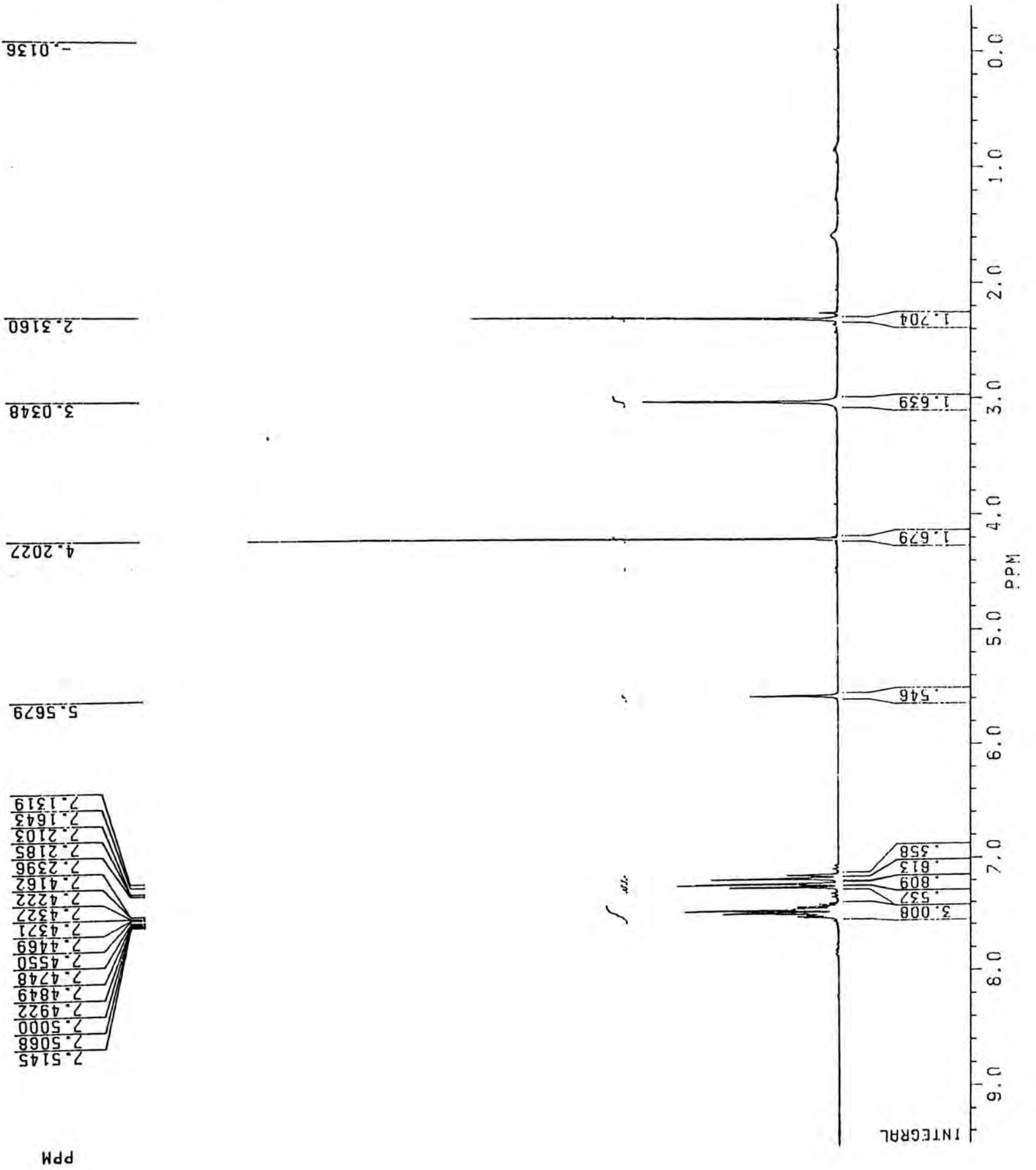
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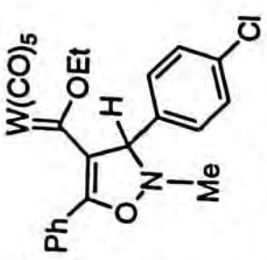
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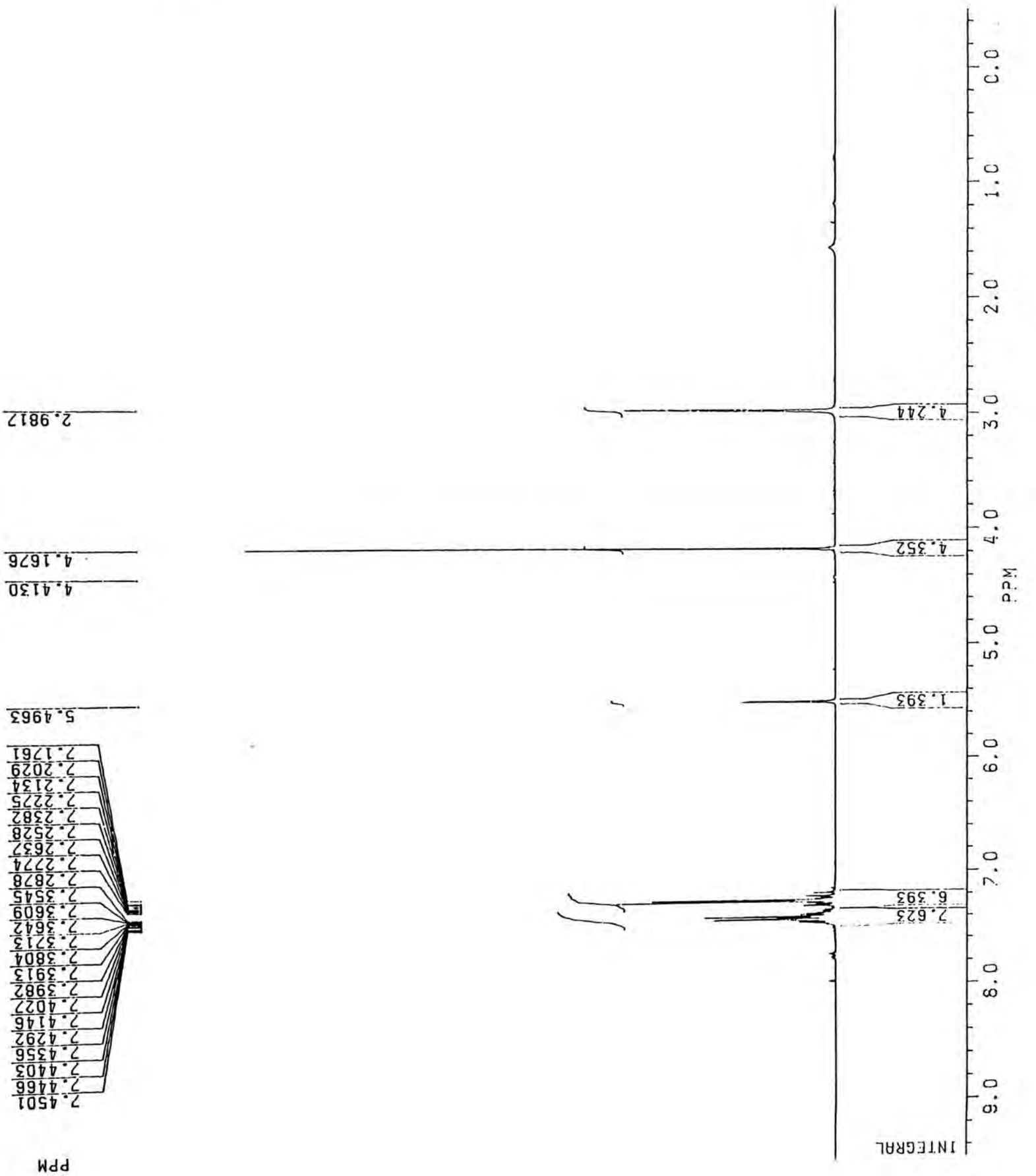
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